

FINAL REPORT

RESEARCH AND DEVELOPMENT OF METHODS FOR THE ENGINEERING
AND CONTROL OF TOXIC AIRBORNE EFFLUENTS

Volume I

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Submitted to the California Air Resources Board
in partial fulfillment of Contract #A4-159-32

June 1987

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PROJECT I

DEVELOPMENT OF AN EXPERIMENTAL PROGRAM IN HAZARDOUS WASTE
INCINERATION

by

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ACKNOWLEDGEMENTS

The authors would like to thank Dr. J.C. Kramlich, Mr. W.S. Rickman, and Dr. L.R. Waterland for taking the time to complete the hazardous waste incinerator evaluation questionnaire. In addition the authors are grateful to Mr. R.A. Brown, Dr. R.C. Flagan, Dr. J.C. Kramlich, Professor C.K. Law, Dr. H.B. Mason, Mr. W.S. Rickman, and Dr. L.R. Waterland for consultations in understanding this complex and interesting subject. The authors gratefully acknowledge the support of the CARB contract manager, Joseph Pantalone. This project was funded by the California Air Resources Board, Contract #A4-159-32.

LIST OF ACRONYMS

APCD	-	Air Pollution Control District
CARB	-	California Air Resources Board
CU	-	Combustion Unit
DE	-	Destruction Efficiency
DOHS	-	Department of Health Services (California)
DRE	-	Destruction and Removal Efficiency
GC/MS	-	Gas Chromatography/Mass Spectroscopy
HWI	-	Hazardous Waste Incineration (or Incinerator)
MM5	-	Modified Method 5 (EPA)
PIC	-	Product of Incomplete Combustion
POHC	-	Principal Organic Hazardous Constituent
SASS	-	Source Assessment Sampling System
TCDD	-	Tetrachlorodibenzodioxin
TCE	-	Trichloroethylene

DEVELOPMENT OF AN EXPERIMENTAL PROGRAM IN HAZARDOUS WASTE INCINERATION

INTRODUCTION

The California Air Resources Board (CARB) is charged with assisting the Department of Health Services (DOHS) and local air pollution control districts (APCDs) in evaluating applications to burn hazardous wastes in a variety of incinerators. Incinerator evaluation tests typically involve determining the destruction and removal efficiency (DRE) of the incinerator for selected principal organic hazardous compounds (POHCs), as well as determining the emissions of certain products of incomplete combustion (PICs). Because these tests require extensive analyses which are very expensive, unanticipated problems with sampling at the test site or subsequently with analytical methods can cause costly delays or require further testing.

The CARB has contracted with the Department of Civil Engineering, UC Davis to investigate the feasibility of developing an experimental program to study hazardous waste incineration. Such a program would be geared toward improving the efficiency of conducting these tests, lowering test costs, and interpreting test results. The desired goals of an experimental program on waste incineration are:

1. To develop and test sampling methods for incineration studies.
2. To perform studies of products of incomplete combustion.
3. To study the effect of mixing of fuels on emissions.
4. To evaluate the feasibility of using surrogate hazardous waste compounds in incinerator studies.
5. To study the influence of various "failure conditions" on the destruction efficiency (DE) of hazardous compounds.

6. To determine the significant operational parameters such as minimum temperature, residence time, oxygen concentration, etc., for effective destruction of hazardous compounds.
7. To determine which surrogate compounds best represent complete combustion of the hazardous waste.

The purpose of this report is to assess the feasibility of the CARB's development of an experimental program in hazardous waste incineration. This study will focus on answering the following questions:

1. What can be accomplished in pilot scale and laboratory hazardous waste incineration studies?
2. What are the advantages, disadvantages, costs, and commitments of the following options:
 - a) CARB designs a test program then contracts for use of an existing facility to carry out the study.
 - b) CARB builds and operates its own facilities to carry out its studies.
3. What laboratory scale studies may be beneficial to CARB's hazardous waste incineration program?

This study will be divided into five sections: I. Benefits and Limitations of Pilot Scale and Laboratory Hazardous Waste Incineration Studies, II. Contracting for Use of an Existing Pilot Scale Hazardous Waste Incinerators, III. Development of a CARB Pilot Scale Hazardous Waste Incinerator, IV. Laboratory Scale Hazardous Waste Incineration Studies, and V. Conclusions and Recommendations.

I. BENEFITS AND LIMITATIONS OF PILOT SCALE AND LABORATORY HAZARDOUS WASTE INCINERATION STUDIES

An experimental program in hazardous waste incineration can be developed on two different levels: a pilot scale or laboratory (bench) scale. Ideally, a complete experimental program in hazardous waste incineration would involve a mix of the above as well as full-scale verification tests.

A pilot scale program in hazardous waste incineration (HWI) would involve the development and/or testing of a pilot scale combustor. In a sense, the pilot scale program involves the testing of a scaled down version of a full scale combustor, with a nozzle, flame zone (i.e. the region characterized by rapid reaction and heat release, temperature increase, and an abundance of radicals), post-flame zone, and effluent. The benefits of a pilot scale program are that the same processes, such as atomization, fuel/air mixing, flame zone destruction, non-flame zone destruction, occur in both the pilot scale and full scale combustors.

The major limitation of any pilot scale combustion device is the uncertainty in scaling of all important phenomena occurring in full scale systems. Specifically, scaling of nozzle performance, fluid dynamics, and heat transfer is extremely difficult in combustion systems (e.g. existence of recirculation patterns near the burner). Based upon interviews with various combustion experts in California, the general consensus is that scaling of full scale systems to a pilot scale for quantitative POHC DE and PIC concentration predictions is not possible at this time. Nevertheless, useful combustion information including chemical kinetic studies, can be generated despite these limitations. It is felt that flame-mode incinerability ranking studies, surrogate studies, failure-mode effects on DE, and some PIC studies can be carried

out effectively at the pilot scale. These pilot scale studies would contribute significantly to the understanding of full scale HWI processes.

An immediate application that could be realized from a pilot or laboratory scale HWI program would be the establishment of a flame failure-mode incinerability ranking of various wastes. Flame failure-mode incinerability rankings complement non-flame zone ranking studies [5] which have been conducted or are currently underway. Because the cost of monitoring every hazardous compound in full scale tests is prohibitive, it is practical to monitor only the most refractory POHCs and PICs. By utilizing flame-mode incinerability ranking in conjunction with non-flame rankings it may be possible to identify refractory compounds for a variety of incinerator failure conditions, including atomizer failure, mixing failure, thermal failure, or quenching failure [9]. Once identified, these compounds may serve as suitable surrogate compounds which can be spiked into the waste to be burned during permitting and compliance tests.

Determination of PICs evolved from the combustion of various POHCs has also been studied using pilot scale HWI experiments [9, 18]. However additional PIC determination tests using pilot scale systems could be of value. In addition, the effectiveness of various compounds for continuous monitoring purposes (SF_6 , CO, THC) in predicting POHC DE and PIC formation could continue to be evaluated.

Laboratory HWI studies also provide an important link in the understanding of the performance of full scale HWI system. Typical studies that can be carried out at the laboratory scale are: droplet combustion studies to study the burning rates and combustion products of various compounds, premixed flame studies in which the chemistry and

chemical kinetics of the combustion of hazardous materials can be evaluated, non-flame studies which evaluate the kinetics of decomposition of compounds in the absence of flames, and flue gas simulation studies in which the effectiveness of source test methods can be evaluated.

In most cases, laboratory studies do not involve scaled down versions of full scale combustors. Rather, one aspect of the HWI process is isolated and studied. The advantage of laboratory studies over pilot scale HWI systems is that a fundamental understanding of the processes that occur in full scale HWIs can be developed under controlled conditions. Additionally, laboratory systems are less costly to obtain and maintain than most pilot scale systems, and require less operator training. The drawbacks are that laboratory systems are further removed from the full scale HWI systems. Thus it is difficult, perhaps impossible to make quantitative predictions of waste destruction based solely on lab scale data.

II. CONTRACTING FOR USE OF AN EXISTING PILOT SCALE HAZARDOUS WASTE INCINERATORS

A questionnaire (Appendix A) was prepared and sent to selected companies in California involved in hazardous waste incineration research to evaluate the potential for CARB renting time on existing pilot scale HWI systems. The objectives of the questionnaire follow: a) to evaluate pilot scale HWI facilities present in California that could be utilized by CARB to perform tests and sampling methods development, and b) to evaluate the possible purchase or construction of a pilot scale incinerator to be operated by CARB personnel. An evaluation of the responses to objective a) are discussed in this section and the responses to objective b) are presented in Section III.

Questionnaire Description

The questionnaire (see Part II of Appendix A) was developed to obtain the following information: a physical and an operational description of the unit, availability and type of computer models used to describe the unit, fuels and SF_6 tracer capability, methods for simulation of failure conditions, and costs of rental and operation of each combustion unit (CU). Information gathered from the physical description questions included firing rates, exhaust gas flowrates, location and number of sample ports, ability to change combustion volume, and data gathering/analysis capabilities. The operational description dealt with questions regarding variability of swirl (proportional to turbulence), flame and wall temperature measurement capabilities, and the states (gas, liquid, solid) of fuel burned. Fuels and tracer capabilities dealt with the range of liquid fuel viscosities usable in the CU, experience burning slurry and solid fuels, and capabilities for SF_6 tracer studies. Information on the ability to simulate failure conditions involving wall/flame quench and atomizer failure were also desired. Potential contractors were asked to estimate costs of using the CU to conduct HWI tests in response to a standard scenario. The standard test scenario assumed that a combustion test lasted for one week (during regular working hours only), and would be performed using one liquid fuel specified by the CARB and supplied by the contractor. In addition, the following failure conditions would be simulated: atomizer failure, wall or flame impingement quench, high and low excess air. Injection ports for SF_6 were to be provided. The contracting company would also provide use of the CU with all personnel necessary for its operation, all combustion process information, and CARB for access to the unit source tests.

Summary of Questionnaire Responses

Responses for seven different CUs consisting of three different types (liquid/gas fired, rotary kiln, and circulating bed CUs) are presented below. To assure corporate confidentiality each of the seven CUs was given a code (CU-A through CU-G). A tabular summary of responses for each of the CUs surveyed is presented in Table 1. What follows is a review of the responses to each group of questions.

The range of firing rates for the CUs varies from 30 to 2500 kBtu/hr for combustion of No. 2 fuel oil, and a corresponding exhaust gas flowrate of 1 to 550 SCFM. Thus CARB's requirement for at least 10 SCFM for sampling purposes is met by all CUs except for the lower ranges of CU-C and CU-D. Because of their higher firing rates test results from units CU-A, CU-B, and CU-E probably have greater applicability to full scale combustors of similar configuration than do the other CUs. The number of sample ports available for post flame temperature determination is adequate for all CUs except possibly for CU-D.

The ability and speed with which the combustion volume of the CU can be changed might be important in performing some residence time studies. All CUs surveyed except CU-C and CU-G reported ability to change combustion volume. The percent CU volume change and time to complete volume change varied widely. For example the volume of CU-B can be reduced to $1/5$ of the original volume, but the change requires one week to accomplish, while the volume of CU-D can be reduced to $2/3$ the original volume in only 1 hour. Obviously the CU size, design, and physical layout influence both the facility and degree of volume change.

The ability to stage combustion air is useful in controlling the combustion process in the flame zone and in the post-flame zone. All CUs surveyed have the ability to stage combustion air except for CU-D

Table 1
INCINERATOR FEASIBILITY STUDY
QUESTIONNAIRE RESULTS

Question	CU-A	CU-B	CU-C	CU-D	CU-E	CU-F	CU-G
Range of firing rates based on No. 2 fuel oil (1000 Btu/hr)	250 to 2000	800 to 2500	30 to 100	40 to 150	800 to 2500	200 to 600	45 to 80
Exhaust gas flowrate with No. 2 fuel oil (SCFM)	50 to 350	150 to 550	6 to 30	1 to 40 (wet basis)	150 to 550	50 to 160 (wet basis)	12 to 22 (wet basis)
Number of sample ports along the post flame region	5 to 10	24	36	1 at exit	18	7	11
Can the CU volume be changed? How long to change? Degree of change?	Yes few days 1/2 sec. residence time per section	Yes 1 week reduced to 20% of original volume	No	Yes 1 hour reduced to 33% of original volume	Yes NA reduced to 80% of original volume	Yes NA NA	No
Can the injection of combustion air be staged?	Yes, at 5 levels. Staged air controlled and measured.	Yes, at any axial location. Staged air controlled and measured.	Yes, at 36 access ports. Separate control and measurement available.	No.	Yes, at 18 ports. Air preheated and individually controlled and monitored.	No.	Yes, at 2 ports.
Data gathering and analysis capability.	Temp., flow rates, press., CO ₂ , CO, NO _x , SO ₂ , TUMC displayed and monitored on real time basis. Plotting and statistics available.	Temp., flows, press., CO ₂ , CO, NO _x , SO ₂ , TUMC monitored continuously. Data collected manually except for emissions strip charts. Plotting and data analysis available.	Temp., flows, press., CO ₂ , CO, NO _x , SO ₂ , TUMC monitored continuously. Data collected manually except for emissions strip charts. Plotting and data analysis available.	Temp., flows, press., CO, CO ₂ , O ₂ , TUMC monitored.	Temp. monitored by computer continuously. Flows monitored manually. CO ₂ , CO, NO _x , SO ₂ , TUMC recorded by strip charts. Data analysis and plotting available.	Temp., press., flows, and CO ₂ monitored and recorded on real time basis automatically. Data analysis and plotting available.	Temp., flows, CO ₂ , CO, O ₂ monitored.
Simultaneous Comb. of liquid/gas fuels available?	Yes.	Yes.	Yes.	Not presently. Could be fabricated.	Yes.	Not presently. Can be fabricated.	Yes.
Gas burner available?	Yes.	Yes.	Yes.	Yes.	Yes.	Yes.	Yes.
Range of swirl numbers for No. 2 fuel oil?	No swirl.	0 to 0.85	Inner: 0 to 22 Outer: 0 to 0.4	0 to 2.4	Some swirl present but not quantified.	0 to 2.5	0 to 2.4
What flame temp. determination technique used?	Type K thermocouples at twenty locations.	Optical & suction pyrometry available. Suction pyrometry and Type R thermocouples used.	Suction & optical pyrometry possible, Type R thermocouples used.	Suction & optical pyrometry possible, suction pyrometry used.	Suction & optical pyrometry possible, Type R and suction pyrometry used.	Suction pyrometry used. Solids temp. determined by two color pyrometer.	Suction pyrometry used.
Post flame temp. distribution?	Yes.	Yes.	Yes.	Yes.	Yes.	Yes.	Yes.

Table 1 (continued)

Wall temperature distribution?	Yes.	Yes.	Yes.	Yes.	Yes.
Computer modeling capabilities.	Uniform temp. distribution heat transfer model and high turbulence permit predicts temp. profiles the use of a simple oxidation kinetic model.	Yes.	Overall DRE predicted using thermal info. generated from 2 D Monte-Carlo radiation heat transfer model.	Equilibrium & kinetic codes available to predict gas specie concentrations as a function of time.	DRE and gas temp. profile predicted using a 2-D radiation heat transfer model.
Is SFA injection available? Where injected?	Yes. Injection in either liquid fuel stream or into burner.	Yes.	Yes. Injection in either liquid fuel stream or into burner. Also injection into air or steam for air/steam atomized nozzles is possible. With dual-fuel nozzle, SFA can be injected with gas.	Yes. Injection in either liquid fuel stream or into burner. Also injection into air or steam for air/steam atomized nozzles is possible. With dual-fuel nozzle, SFA can be injected with gas.	Yes. Can be injected in the air side of dual-fluid nozzle or near nozzle tip.
Can flame impingement on a cold wall and cold wall quench be simulated?	Cold wall quench available.	Yes for both.	Yes for both.	Yes for both.	Flame impingement on a cold wall available.
Can atomizer failure be simulated?	Not applicable.	Yes.	Yes.	Yes.	Yes.
Cost per week for test including: fuel, permits, process rate info. Excluding special set-up costs, i.e. addition of cold wall quench, etc.)	\$60,000	\$10,500 for 1 week test \$10,000 for post test costs.	\$6500 for 1 week. \$6000 for post test costs	\$10,500 for 1 week, \$10,000 post test costs.	\$9000 \$6000

and CU-E. Control of the wall temperature in the post-flame region is another important attribute of a research CU. If the wall temperature can be controlled, then time-temperature studies of the post-flame region can be conducted. If the post flame region is cooled, then post flame reactions are quenched and analysis of effluent gases shows flame zone processes only. CU-B is equipped with heating coils filled with high temperature heat transfer fluid, permitting the specification of time-temperature of post flame gases. CU-C and CU-G are back-fired so that heat losses in the post flame region are reduced. CU-D has cooling coils available for quenching of post-flame reactions.

The data gathering and analysis capabilities of the various CUs varied widely. In all cases, temperatures, pressures, flows, and common combustion gases are monitored. CU-A and CU-F have automatic real-time data collection for all measured parameters while the other CUs have manual data collection. Data plotting and statistical analysis of combustion data are available for CUs A, B, C, E, and F.

All CUs surveyed were able to burn gaseous fuels. Simultaneous combustion of liquid and gaseous fuels is presently available in all CUs surveyed except CU-D and CU-F. Fabrication of a burner to permit the simultaneous combustion of gaseous and liquid fuels is possible for CU-D and CU-F.

Swirl is often used to modify flow characteristics in liquid fuel burners. A swirl number may be defined as the ratio of the jet angular momentum to the jet linear momentum (13). Thus an increase in swirl number corresponds to an increase in turbulent mixing. Swirling flows result in intense recirculation patterns and increased swirl is found to shorten the length of the flame zone while increasing the length of the post-flame zone. All CUs except CU-A are capable of

varying the burner swirl, with CU-B offering the smallest range of swirl variation and CU-C permitting the largest range of swirl variation.

Techniques to measure flame temperature include optical pyrometry, suction pyrometry, and the use of thermocouples. Suction pyrometry is used for flame temperature determinations of CUs B, D, E, F, and G. Thermocouples are used in CU-A and CU-C to determine average flame temperatures. Ports for the use of either optical or suction pyrometry are available for CUs B, C, D, and E. The temperature of solids in CU-F is determined by using a two-color pyrometer. Both post-flame and wall temperature distribution data are available for all CUs surveyed.

All of the companies surveyed had developed modeling capabilities for their CU except for CU-A. However, because of a nearly uniform temperature distribution, a high degree of turbulence, and plug-flow characteristics of CU-A, a simple kinetic model might be developed to successfully predict species DE. Models for all of the other CUs involve determination of the temperature distribution using heat transfer models and then application of kinetic and equilibrium codes to predict specie concentrations.

In the combustion of liquid fuels, the fuel viscosity is an important parameter in governing the performance of the CU. For the CUs surveyed, the range of kinematic viscosities varied from 30-100 seconds, Saybolt Universal (SSU) for CU-E to 30-900 SSU for CU-B and CU-C (water at 20°C has a kinematic viscosity of 30 SSU). Liquid fuel preheating would be used to reduce the fuel viscosities of heavy fuels and is available for CUs, B, C, D, F, and G.

The capability of burning solid fuels and slurries is a desirable option for a HWI pilot scale program. Although considerable data have been generated on liquid hazardous wastes, much less comparable data are

available for combustion of hazardous solid wastes or slurries. All CUs surveyed except CU-D reported either solids and/or slurry combustion capability. CU-F has the capability of firing containerized waste while CU-A is capable of firing solids and slurries with a particle diameter of up to 1 inch. CUs B and E can fire slurries with a particle diameter less than 100 micrometers using a pressure-atomized nozzle and up to 200 micrometers using an air-atomized nozzle. Slurries with a particle diameter less than 100 micrometers can be burned in CU-C using a pressurized nozzle. The use of an air-atomized nozzle in CU-C permits the use of slurries with particle diameters larger than 100 micrometers. Note that the combustion of high ash fuels in CU-C may require continuous removal of bottom ash, which is not in the current design. Slurries with particle diameters less than 300 micrometers can be burned in CU-G. A partial list of the fuel mixtures previously tested in each CU is presented in Table 2.

The injection of SF_6 has been proposed as a surrogate for DE monitoring of HWI facilities. All CUs surveyed reported capabilities of SF_6 (or some other gaseous tracer) injection into the CU. Injection of SF_6 can take place in several ways: a) into either the liquid fuel stream or into the burner for CUs A, B, C, E; b) into the air or steam for air/steam atomized nozzles in CUs B, C, E; c) with the gas in a dual-fuel nozzle in CUs B, C, D, E, G; d) near the nozzle tip in CUs D and G; and e) near the burner in CU-F.

The importance of examining the effect of failure conditions on DE has been discussed. Both flame impingement on a cold wall and cold wall quench can be simulated in CUs B, C, D, and E. Cold wall quench can be simulated in CU-A and flame impingement on a cold wall can be simulated in CUs F and G. Atomizer failure can be simulated in all CUs except for

Table 2
FUEL MIXTURES PREVIOUSLY TESTED

CU-A	CU-B	CU-C	CU-D
Rubbish	Coal-oil	Heavy fuel oil	Various liquid
Diatomite	mixtures	Various liquid	fuels
High-cyanide, fluoride pot linings	Solid/liquid forms of solvent refined coal	forms of solvent refined coal	
Chlorinated hydrocarbons	No.2 fuel oil w/ chlorobenzene, carbon tetra-		
High sulfur coke	chloride, chloro-		
Chlorinated solid wastes	form, methylene chloride,		
Chlorinated coke residue	dichloroethane		
Bark	Mixture of 70%		
Wood wastes	methanol, 20%		
Oil shale	water, 5%		
Uranium-oil slurry	methylene chlor- ide, 5% chloro-		
Coal refuse	form & chloro-		
High nitrogen cow manure	benzene		
High chlorine oily bilgewater			
High phosphate, boron, nitrogen, oil slurry			
CU-E	CU-F	CU-G	
RDF and pulver- coal	Various liquids, sludges, and	Various slurried fuels	
Pulverized solid solvent refined coal	solid container- ized wastes	Pulverized coke emulsified in water	

CU-A, which doesn't have an atomizer.

The costs of renting a CU varied widely among the CUs surveyed. The cost estimates presented below are based on the following assumptions: a) a test period of one week (Monday to Friday), b) one contractor supplied liquid fuel (specified by CARB) to be used during the entire week, c) the following failure conditions would be simulated if applicable: atomizer failure, wall or flame impingement quench, high excess air, low excess air, d) SF_6 injection port, e) contracting company must provide access to the CU for a source test and all necessary personnel for its operation and data collection, f) CARB will gather samples during regular working hours only. The rental costs ranged from a low of \$6000/week for CU-D and CU-G to a high of \$60,000/week for CU-A. For CUs B, C, E, the rental costs (which include personnel for CU operation, equipment use fees, fuel) were presented along with post-test costs (which include data reporting, returning facility to base configuration, etc.). The post-test costs are not specified but are estimated to be as much as a single week of testing. Note that the one week rental cost for CUs B, C, E, does not include extra costs for facility set-up and preparation (which are highly project specific and are estimated to be as much as a single week of testing). Thus for CUs B, D, E, the total cost charged to CARB for one week of testing may be 2 to 3 times the quote for the one week use fee. Therefore, the effective cost for one week of testing is \$20,000 to \$30,000 for CU-B, \$13,000 to \$19,000 for CU-C, and \$21,000 to \$30,000 for CU-E. The estimated cost for CU-F is \$9000/week. It must be noted that quoted costs are not bid costs, but rather estimates based upon the companies' experience or projections.

III. DEVELOPMENT OF A CARB PILOT SCALE HAZARDOUS WASTE INCINERATOR

To evaluate the feasibility of the CARB building and operating a pilot scale HWI incinerator, Part III of the questionnaire shown in Appendix A was sent to selected companies in California involved with HWI research. Descriptions of three different pilot scale combustion systems were submitted for evaluation in response to the questionnaire. In this section of the study, the goals of Part III of the questionnaire and a summary of the major features of each of the proposed pilot scale systems submitted are discussed. All company names have been omitted and the order of presentation was selected randomly.

Questionnaire Description

The major goal of Part III. of the questionnaire was to obtain information on small scale CUs that could be used for a CARB operated hazardous waste incineration research program. Specifically, information on a CU nominally rated at 70 to 150 kBtu/hr burning No. 2 fuel oil was desired. Burner requirements included the capability of burning liquid fuels within a range of viscosities (No. 2 fuel oil to toluene) and slurry fuels, at various swirl settings. A capability of simulating various failure conditions was also required: low/high excess air, wall quench, and atomizer failure. To permit variation of the combustion volume, a modular design was also desired. All controls and appurtenances necessary for operation and monitoring of the CU were included except for gas analysis and data acquisition equipment. A method for injecting SF_6 into the CU was also required. To assure complete destruction of all hazardous products, independent of the operation of the CU, an afterburner section was also required. The total cost of the system was based on turn-key installation and was to include operator

training. The uncertainty of the cost estimate and the delivery time for design, construction, installation, and shake-down testing was also requested.

CARB Pilot Scale CU#1

The first CU discussed in this section closely simulates the capabilities of CU-D, discussed in the previous section. CU#1 is designed to simulate processes that occur in the flame zone of liquid injection incinerators. Features include high efficiency operation, small size, and an ability to simulate failure conditions.

Physical description: CU#1 is a liquid injection combustor with chamber dimensions of 12" ID by 36" length. A sketch of the system is presented in Figure 1. Two nozzles can be utilized in this CU. The first is a hollow-cone type with a 60 degree spray angle which cannot be used for slurry fuels. Various sizes permit fuel rates of 0.5, 0.75, 1.0, and 1.5 gal/hr. Slurry fuels can be tested utilizing a twin-fluid nozzle which uses a high pressure air stream to atomize the slurry. A swirl block generator is used to obtain swirl numbers ranging from 0 to 2.4. Vanes on the swirl block generator are mechanically adjusted.

A castable refractory cone in the combustor provides a smooth transition between the burner and combustor, preventing recirculation cells from forming. Four view ports are available for flame observation, sampling in flame zone, or flame temperature determination. The body of the combustor consists of three sections of flanged double-walled stainless steel tubing. Cooling water is circulated between the inner and outer tube walls to control the wall temperature. The flanged sections are interchangeable and yield volume changes of 0.8 cu. ft.

A nitrogen pressurized feed system is used to deliver liquid fuel

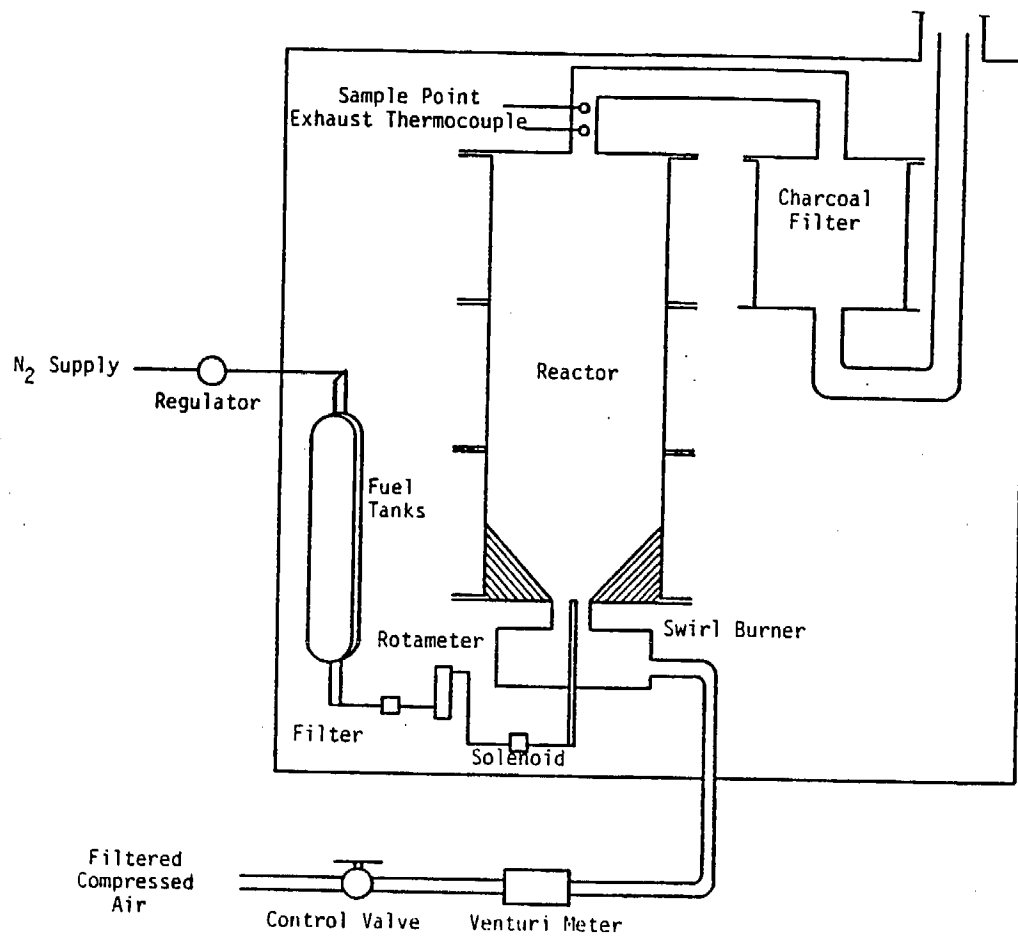


Figure 1. Schematic diagram of CARB Pilot Scale CU #1.

to the burner without pulsations, which could otherwise occur with mechanical pumps. A solenoid provides remote shutdown capabilities in the event of a power failure or other emergency.

The combustor is placed within a fume hood which is continuously vented. In place of an afterburner, a large charcoal filter canister is used to collect trace organics. A small HCl scrubber follows the charcoal filter.

Features: Five failure modes can be simulated with this CU. High and low excess air failure modes can be simulated by variation of the air flowrate. The wall quench failure mode is ideally suited for this CU because it is designed to study flame reactions. Water cooled walls are used to quench undesired post-flame reactions. Flame impingement can be simulated by insertion of a water-cooled coil into the flame zone. To simulate an atomizer failure, an oversized nozzle can be used to create large fuel droplets of low momentum. An aerodynamic failure (which changes the interaction between the air and fuel) can be simulated by changing the burner air velocity, swirl number, or the spray angle.

SF₆ can be introduced into an annular space in the burner between the fuel and combustion air. Injection of SF₆ into the liquid fuel stream could cause an atomizer failure condition (as the SF₆ can form gas pockets) and therefore was not recommended.

Schedule: The proposed facility would require about four months to complete; including design, fabrication, installation, shakedown, and operator training.

Budget: The proposed facility would cost about \$65,500 +/-10%.
This cost includes the following:

- Compressor, Chiller, air tank
- Reactor air cleaning, metering and control system
- Cabinet for reactor with vent blower
- Fuel storage tanks, filters, controls, meters
- Selection of pressure atomizers
- Combustor body, three sections with quarl and end plates
- Swirl block generator
- Charcoal trap for flue gas exit
- Thermocouples for flue gas and cooling water
- Slurry pumping system with twin-fluid nozzles
- SF₆ injection system
- Auxiliary hardware and electrical supplies for installation

Comments: The company submitting this system had some comments which relate to the proposed HWI research program. They noted that good hardware does not necessarily imply cost effective research. Therefore to assure that a quality research program is developed they recommend that operational and supervisory personnel be intimately familiar with the design and construction of the combustor. In addition, they recommend that vendor technical staff provide 1) on-site training of CARB personnel, and 2) on-site start-up and shake down of the equipment.

CARB Pilot Scale CU#2

This CU is designed to meet all of the specifications outlined in part III of the questionnaire. This CU allows for staged construction of a sophisticated facility by adding on to a base facility, which is outlined in this section.

Physical description: The physical description of this CU is described in seven parts dealing with main combustor, burner, air flow control and measurement, fuel delivery, gas cleanup and cooling, controls and safety features, and operator training. A sketch of the main features of CU#2 is presented in Figure 2.

The main combustor of CU#2 is vertically down-fired which permits combustion volume changes (assuming an overhead crane is available). The dimensions are 10" ID by 10' long with 16" of layered insulation. Based on these dimensions, a temperature profile varying between 2800°F to 1500°F and a residence time of 3 seconds can be achieved. To accommodate combustion volume changes, the main combustor can be divided into modular sections of 2' and 3'. Samples ports can be spaced at intervals of 6". An afterburner, 7' in length, is horizontally mounted at the elbow of the exit from the main combustor (see Figure 2). Gases exiting the afterburner rise vertically, are cooled naturally (i.e. no mechanical cooling device is utilized), and pass through an ID fan.

The burner system used in CU#2 is a small research dual register burner which permits the control of air mixing and burner swirl. This burner has interchangeable fuel nozzles which allow for study of atomization failure studies. A commercial oil burner could be utilized for certain studies at considerable savings over a research burner, but with much less flexibility. A conventional commercial gas burner is used for the afterburner.

The air flow control and measurement system is designed around the assumption that house compressed air at 100 psi is available in sufficient quantities for primary and staged combustion air, and atomization air.

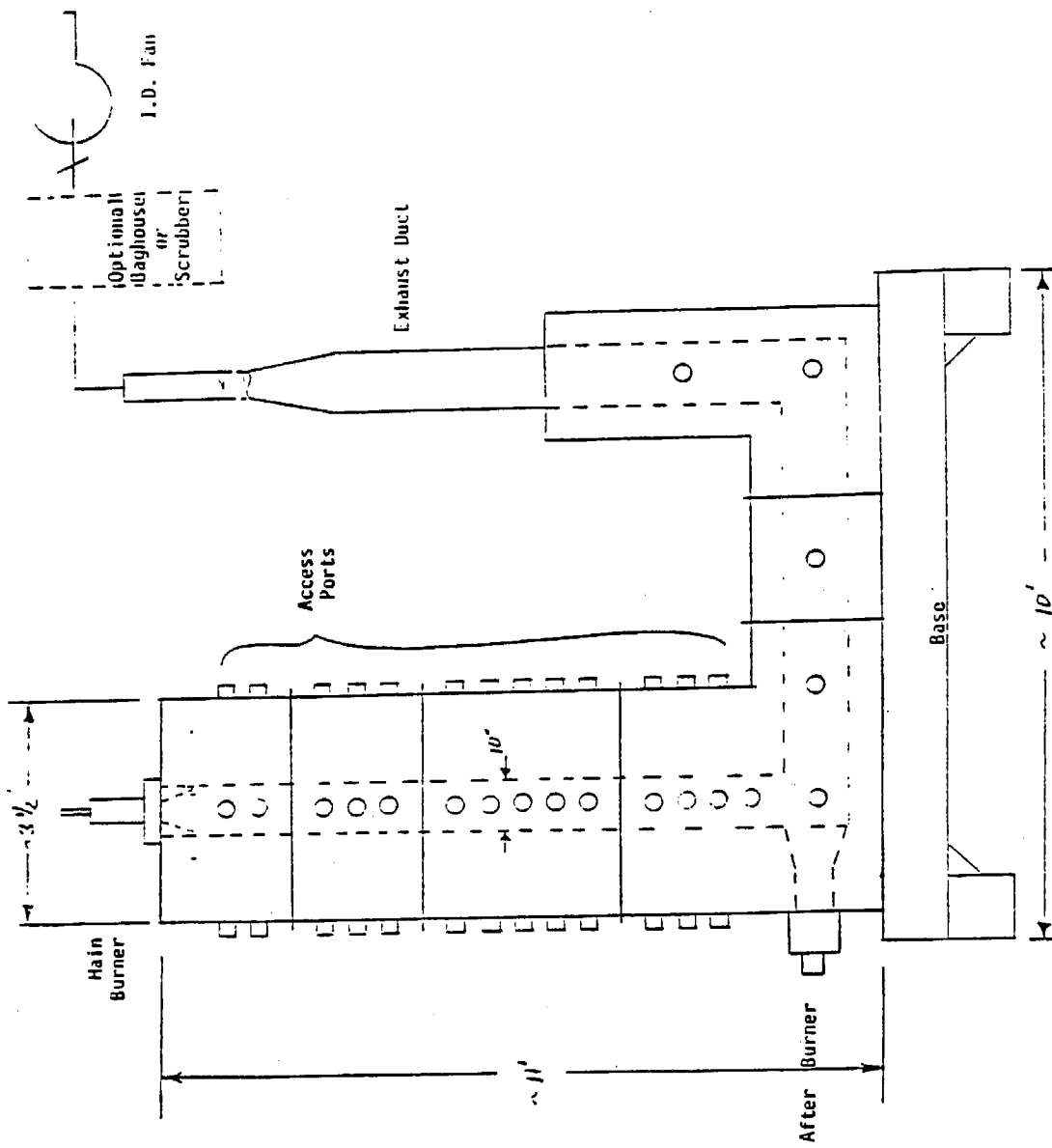


Figure 2. Schematic diagram of CARB Pilot Scale CU#2.

Three fuel delivery systems are utilized in CU#2. The first is a natural gas system which is used for liquid fuel heating (to reduce viscosity as needed) and for the afterburner. The second fuel delivery system is the fuel oil system which consists of pump pressure relief valve, flowmeter, safety shutoff valve, line purge tap, and pressure regulating valve. Air-atomized nozzles are used, permitting a turndown ratio of 3:1 or less. The slurry fuel delivery system consists of a slurry pump, heated tank with stirrer, weigh scale to determine flowrate and flow control valve. Special air-atomized or rotary-cup nozzles are required when firing slurry systems. SF_6 can be added to each of the fuel delivery systems.

No active gas cooling system is used in this design. A small water scrubber is used to clean up particulate matter and to remove HCl and SO_3 from the flue gases.

Manual controls are used in this design. The only automatic feature is the flame safeguard system which controls the pilot sequencing and solenoid valves for the main burner fuel and the afterburner gas. U-V flame detectors are used to sense the flame. This system permits unattended overnight operations. A centrally located panel contains all rotameters, control valves (except gas), temperature readout, and flame safeguard.

Operator training of one week follows installation, start-up, and checkout. Operating personnel should be present to assist in installation and start-up of the CU.

Features: Four failure modes can be simulated with CU#2 including: high and low excess air failure, flame impingement on a cold surface, atomizer failure, and aerodynamic failure. As noted earlier, SF_6 can be injected into the fuel line.

Schedule: The proposed facility would take approximately seven months to complete: design - 2 months, fabrication - 3 months, installation and checkout - 2 months.

Budget: The proposed facility would cost about \$150,000 +/- 10%. The cost estimate is broken down into the following categories:

Main combustor and support	\$58,000
Burners	9,000
Air flow control and measurement	10,000
Fuel systems	24,000
Gas cleanup and cooling	6,000
Control and safety	36,000
Operator training	7,000
TOTAL	<u>\$150,000</u>

CARB Pilot Scale CU#3

The CU discussed in this section is a scaled down version of CU-A presented in Part II of this report.

Sizes of two pilot-scale CUs, one rated at 70,000 Btu/hr and the other rated at 2 MMBtu/hr, are discussed briefly. The internal diameters of these CUs are 3" and 16" respectively and 12" thick refractory is required. Because auxiliaries such as analyzers, controls, and platforms are independent of the unit throughout, there is not a corresponding order-of-magnitude cost savings with the smaller unit. For example, the 2 MMBtu/hr unit would cost about \$1,000,000 while the 70,000 Btu/hr unit would cost about \$600,000. Turnkey operation can be provided in 10-12 months.

It is also important to note that this company is installing a 2 MMBtu/hr unit in Canada. The Canadians are budgeting for a staff of 12

to run it on a long term, around-the-clock basis. Thus, installation of this CU represents large on-going resource commitments. Nevertheless, this unit has a number of potentially attractive features such as its potential as a low NO_x incinerator, the range of fuels that it can handle, and the possibility that units of this type might become more widespread as "onsite" disposal units.

IV. LABORATORY SCALE HAZARDOUS WASTE INCINERATION STUDIES

As noted previously, laboratory or bench scale combustion studies can provide useful information toward the understanding of major processes that occur in hazardous waste incineration. In this section, four different studies involving HWI, that can be carried out at the laboratory or bench scale will be evaluated with regard to their usefulness to CARB's stated program goals. The laboratory studies discussed in this section are: Combustion Studies of Liquid Hazardous Waste Droplets, Flame-Mode Global Kinetic Studies, Non-Flame Thermal Decomposition Studies, and Flue Gas Simulation Chamber Studies.

Combustion Studies of Liquid Hazardous Waste Droplets

Many liquid hazardous wastes are suitable for burning in liquid-fired boilers and incinerators. Because liquid spray combustion systems are widely used in both boiler and incinerator systems, spray combustion of hazardous waste needs to be evaluated to determine the difficulty of destroying compounds, to predict DE, and to predict the formation of PICs. The study of the behavior of the combustion of liquid hazardous waste droplets provides important information which can be used in spray combustion studies.

Spray combustion involves three basic processes: formation of droplets, heating and vaporization of droplets, and kinetically depen-

dent ignition and combustion of vapor. The spray combustion process is complicated by the nature of convective momentum, heat and mass transfer between droplets and the surrounding gas phase. Turbulence governs interactions between droplets and the gas phase. To obtain a full understanding of the processes involved in spray combustion it is necessary to have a knowledge of a) the mechanism of combustion of the individual droplets that make up the spray, b) the description of the droplets that make up the spray with regard to size and spatial distribution, and c) any interaction between the individual droplets as they undergo combustion in the spray [19].

Studies on the nature of single droplet combustion were started over 30 years ago by Spalding [17] and Godsave [8] with the development of the "d²-law". The d²-law basically states that the surface area of a droplet decreases linearly with time, subject to a number of simplifying assumptions. The d²-law has been a useful model because it also predicts that the flame-front stand-off ratio ($r_{\text{flame}}/r_{\text{drop}}$) and the flame temperature are system dependent constants, independent of the droplet size [10]. Current studies of symmetric droplet burning are targeted toward understanding transient droplet heating, multi-component fuels, variable gas phase transport coefficients, fuel vapor accumulation, micro-explosion phenomena, and finite chemical reaction rates [11].

Some experimental evidence indicates that spray combustion in most practical burners is not the combined effect of many individual burning droplets [2]. It appears that group combustion of droplet clouds is the predominant mechanism in spray burning systems, except for very dilute sprays. However, it has been shown recently that cloud lifetime and cloud ignition/extinction are related to the corresponding results from

droplet burning studies [16]. Thus, droplet burning studies provide an important key to understanding what goes on in spray combustion processes.

A laboratory scale droplet combustion system is conceptually very simple; consisting of a droplet generator, premixed burner, optical analysis equipment, combustor body and accessories (see Figure 3). A laboratory scale droplet combustion system could provide information on six areas summarized below.

Burning and vaporization rate studies: Single droplet quasi-steady state theories predict that the surface area of a burning or vaporizing droplet decreases linearly with time. The d^2 -law is the basis for several spray combustion models [19]. Combustion theories predict that the burning rates of droplets in a cluster (droplets in close proximity to one another) burn at a lower rate than the burning rate of isolated droplets due to competition for heat for vaporization and oxygen for combustion [11]. Thus by comparing the burning rates of isolated droplets with the burning rates of clusters of droplets, one can determine an efficiency factor which can be used in spray combustion modeling. Vaporization studies, which are useful in spray combustion models, can be conducted in the droplet burning apparatus.

Ignition delay time: The ignition delay time is the result of droplet heating prior to ignition. The droplet burning time and the ignition delay time determine the droplet lifetime, which directly correlates with burning time in sprays.

Extinction of burning droplets: An important phenomenon in the study of single droplet burning involves the phenomenon of extinction of the burning droplet. Burning droplets are found to extinguish when a critical "extinction" diameter is attained. Extinction of a single burning droplet occurs when heat is lost to the ambience more rapidly

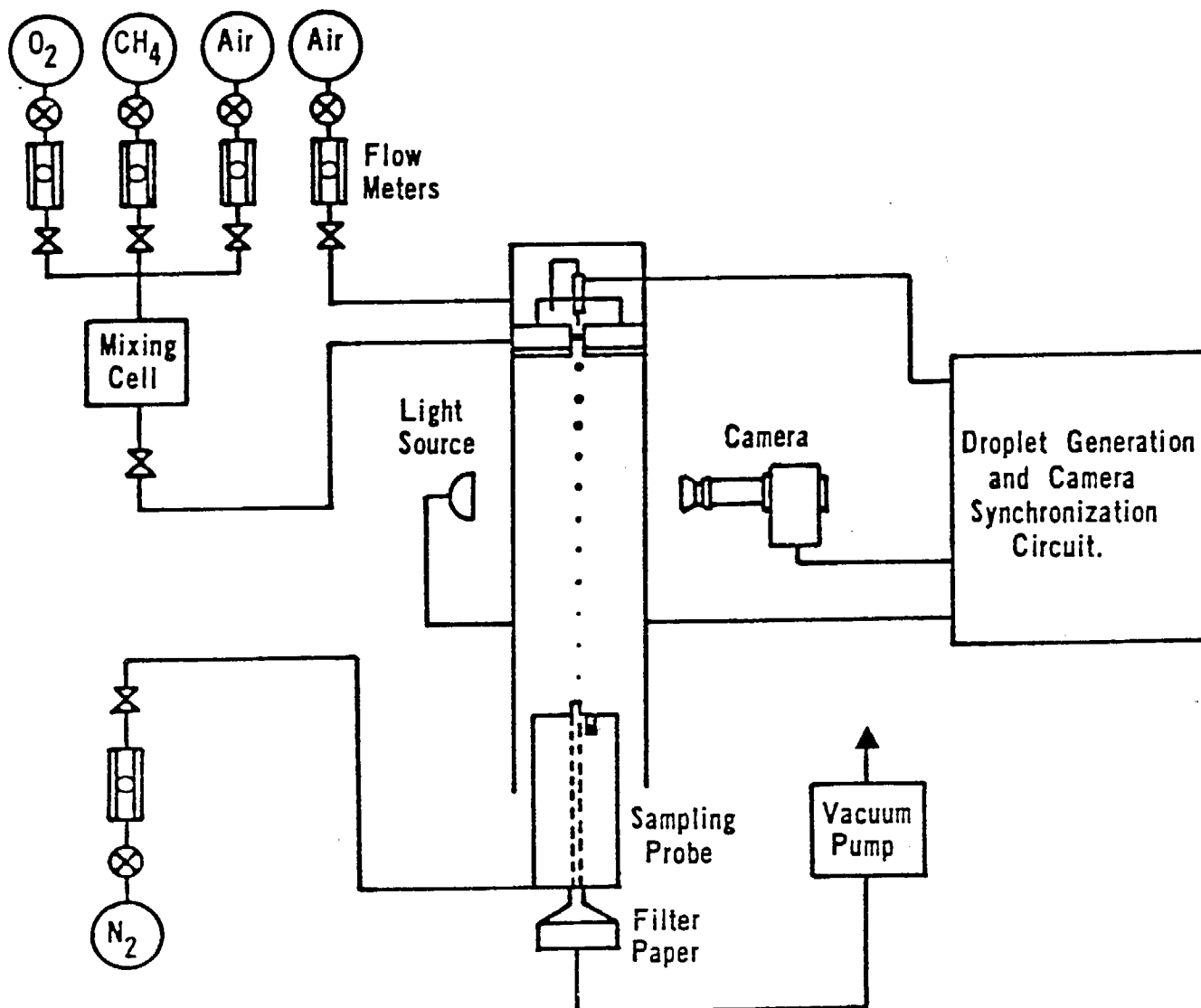


Figure 3. Droplet combustion system.

than it is generated in the flame zone. The extinction diameter is a function of the local ambient oxygen concentration, fuel properties, " d^2 " burning rate, and transport coefficients (and pressure in non-atmospheric burner applications). Because there is always a non-zero extinction diameter, a finite amount of fuel will always escape the flame environment. Thus, the extinction diameter is directly related to DE for single drop studies. Sampling of the products at extinction could provide useful insight into PIC formation. Chung and Law [3] were able to experimentally determine the overall or global activation energy of the burning of decane in air by measuring the droplet and flame diameter at extinction, oxygen concentration at extinction, and the " d^2 " burning rate. Thus chemical kinetic information (global activation energy) can also be obtained from studies of single droplet burning at extinction.

Microexplosion of droplets: Microexplosion phenomenon can occur in droplets of multi-component fuels with widely different vapor pressures. The basic mechanism responsible for a microexplosion event is the diffusional entrapment and volatilization of the lower boiling components in the droplet's inner core. The rapid boiling of the volatile component in the droplet core causes the core to rupture and form very small droplet fragments which are easily volatilized and burned [10]. Present designs of spray systems emphasize the production of optimum droplet size distributions such that the droplets are both large enough for penetration into the combustor interior, and small enough for rapid gasification. However, if microexplosions could be controlled to occur after penetration had been achieved, then rapid gasification need not be a primary concern in designing spray systems. In this manner, large scale mixing can be achieved through spraying and penetration of large

droplets, followed by essentially instantaneous gasification and local mixing through microexplosion [11]. Thus microexplosion phenomena, properly applied, might greatly improve the DE in HWI systems or minimize potential effects of atomization failure. Conversely, waste mixtures may alter the design droplet distribution and an understanding of this process would also have utility.

Sampling of droplet combustion products: Because of the highly controlled conditions in the droplet combustor, sampling of combustion products around individual droplets has been carried out to determine sooting properties of certain fuels [15]. It is possible to use a similar apparatus to determine combustion products from burning droplets of hazardous waste, which would then provide insight on PICs evolved from the combustion of various hazardous wastes.

Ranking of incinerability: An alternative method of ranking incinerability based on a combination of droplet burning rate, droplet extinction diameter, and ignition delay time, could be useful in determining difficult to destroy hazardous wastes. The effect of fuel/waste composition could readily be studied. Such studies applied to flame-mode induced failures and combined with non-flame ranking schemes could provide a firmer basis for selection of surrogate "spike" compounds.

Thus, droplet burning studies could provide much useful information on a fundamental level that may be used to better understand the operation of full scale HWIs. The development of a laboratory scale droplet combustion system would cost about \$10,000, assuming plans were available. Burning rate data and perhaps some extinction data could be produced after about 6 months of full time laboratory work.

Flame-Mode Global Kinetic Studies

Chemical kinetics plays an important role in much of the combustion-phenomena relevant to HWI. Ignition extinction phenomenon, POHC, DE, and PIC production are governed by chemical kinetics. Two important classes of chemical kinetics that occur in HWI are flame-mode kinetics and post-flame kinetics. The flame-mode kinetic studies govern the behavior in the flame while the post-flame (or thermal decomposition) kinetics describe the post-flame region in a combustor. Thus it is important to develop a thorough understanding of both flame and post-flame kinetic mechanisms that occur in the burning of HW in full scale incinerators. Flame-mode kinetic studies are discussed in this section and post-flame kinetic studies are presented in the following section.

Unfortunately, there have not been many flame-mode combustion kinetic studies of HWI to date. A flame-mode kinetics study of trichloroethylene (TCE) was performed by Bose and Senkan [1]. In this study, a flat flame burner was utilized to determine stable species and temperature concentration profiles associated with a TCE/air flame. Based on the results of this study, a two-stage mechanism of the combustion of chlorinated hydrocarbons was developed. Other kinetic studies involving hazardous waste have been conducted utilizing flame inhibitors (brominated and chlorinated compounds). In general, kinetic data availability is limited with respect to the variety of compounds and temperature ranges. Therefore work on flame-mode decomposition of various compounds should be performed to provide more fundamental combustion knowledge. Flame-mode chemical kinetic data could be utilized in the development of global kinetic models for flame-mode decomposition of selected POHC streams.

High temperature flame-mode global studies can be conducted using a

flat flame burner in a laboratory. Fristrom and Westenberg [7] describe an experimental methodology that is utilized for the determination of the net reaction rate of any species in a flame. Stable species and temperature profile data are collected and used to generate continuous profiles utilizing numerical curve fitting routines. Species fluxes are obtained from the first derivative of the continuous species profile. Using the appropriate diffusion coefficients, species fluxes, and mass average velocity, the net reaction rate K_1 is determined according to:

$$K_1 = \frac{P_0 V_0}{M_1} \frac{dG_1}{dz}$$

where:

K_1 = net reaction rate of species 1, moles-cm⁻³-s⁻¹
 P_0 = reactant density (g-cm⁻³)
 V_0 = reactant velocity (cm-s⁻¹)
 M_1 = molecular weight of species 1 (g-gmol⁻¹)

$\frac{dG_1}{dz}$ = species mass flux (cm⁻¹)

Because the determination of G_1 involves the first derivative of the experimentally determined species profile, K_1 is a function of the second derivative of G_1 or experimental species profile data. Dependence on the second derivative of experimental data is a large and unavoidable source of error, requiring highly refined sampling and chemical analysis techniques to obtain meaningful data [7].

To complete the model, one must assume a kinetic form. The Arrhenius form is usually postulated. Global kinetic models (one-step) are relatively simple while detailed kinetic models (multi-step) are

very complicated. If a single step, multi-component model is used we have:



$$K_{\text{POHC}} = -[\text{POHC}]^a [\text{OXIDANT}]^b A \exp[E_a/RT]$$

In this mode, there are four unknowns (a, b, A, E_a) and three pieces of experimental data required ($[\text{POHC}]$, $[\text{OXIDANT}]$, T). Thus to solve for the unknowns, a minimum of four sets of experimental flame data (obtained by varying either temperature, pressure, or mixture composition) are required. Using the values of a , b , A , and E_a determined experimentally, one can predict K_{POHC} given T and the initial concentrations. It must be emphasized that the model determined above is correct only if the reaction mechanism chosen (single or multi-step) is correct. Thus if a multi-step reaction mechanism is proposed, the number of sets of flame data needed to determine the constants increases dramatically.

An apparatus that can be used for studying diffusion and premixed flames is an opposed-jet burner. A schematic diagram of a typical opposed jet burner is presented in Figure 4. Streams of fuel and oxidizer are introduced in opposed and balanced streams. Because the burned gases leave the system radially, the burner axis is usually oriented vertically to preserve the symmetry of the flame. Excellent flat flames can be obtained using an opposed-jet burner if uniform velocity streams are employed [7].

Although opposed-jet diffusion burners are not as common as other experimental burners, they are certainly not a unique or unusual apparatus in combustion research laboratories. Costs for construction of an opposed jet burner vary widely with machine shop costs and availability.

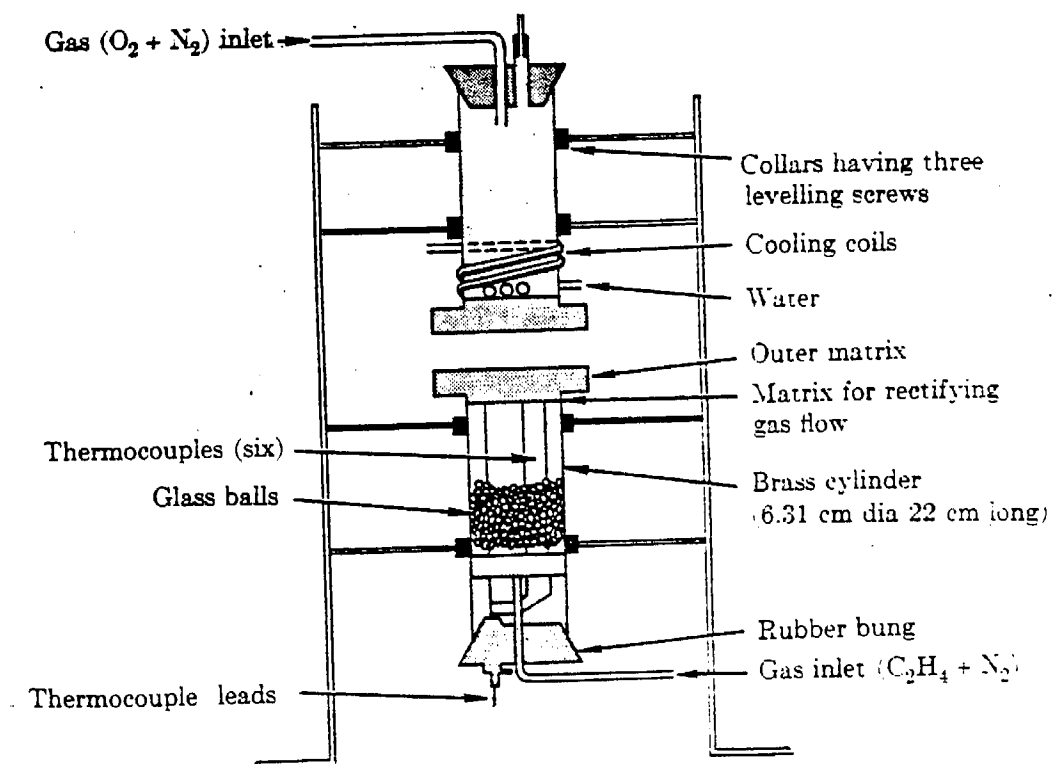


Figure 4. Opposed-jet diffusion flame burner (14), obtained from (7).

However, it is estimated that an entire opposed-jet diffusion burner system could be constructed for about \$10,000, excluding all sample analysis equipment. Because these studies require very sophisticated sampling techniques, it is estimated that 1-2 years would be needed to develop sufficient skill to generate good flame structure data. It must be emphasized that the results from this study cannot be used to predict global DE in full scale combustors because transport properties are not considered. However, flame-mode chemical kinetic data may provide an additional, complementary ranking methodology to those proposed previously.

Non-Flame Thermal Decomposition Studies

Non-flame thermal decomposition studies have been used to determine decomposition profiles of many POHCs under a variety of conditions. Work in this area is being carried out by Dellinger et al. [6] and Lee et al. [12]. The major difference between flame and post-flame reactions involves the presence of radicals (e.g., O, H, OH) in flames. In the post-flame region of the incinerator, these radicals are present at greatly reduced concentrations and thus collisions of energetic molecules govern decomposition rates of POHCs. The results of non-flame studies describe, to a certain extent, what occurs in the post-flame region of a combustor.

It has been argued by Dellinger et. al. [5] that an incinerability ranking scheme based on non-flame thermal decomposition data is highly relevant to monitoring of full scale combustors. It is clear that any POHC not destroyed in the flame zone will be destroyed in the post flame region of the combustor to some extent. If the flame-mode DE of all compounds were equally high in a given test, say 99.999% or higher,

one can infer that an overall DE of less than 99.999% means that part of the fuel did not experience the flame environment and was instead governed by post-flame destruction mechanisms. It is therefore proposed that because all compounds are destroyed with very high efficiency in the flame environment, the most relevant incinerability ranking system is one that predicts thermal stability in the post-flame environment.

The experimental apparatus used by Dellinger et al. [6] to generate non-flame thermal decomposition data consists of a thermal decomposition unit and an in-line GC. The sample is introduced into the system and gradually vaporized in a dry flowing gas stream (e.g., nitrogen, air, or nitrogen/oxygen mixtures). The vaporized sample passes through a controlled high-temperature tubular reactor where it undergoes thermal decomposition. The products evolved from the thermal decomposition of the compound and the remaining parent compound are swept into a high-resolution GC for analysis. The sample insertion chamber, the reactor, and the entire transport system are fabricated of fused quartz to minimize interaction with the sample.

The data resulting from this work are thermal decomposition profiles showing DE versus temperature for various residence times. Thus $T_{99}(t)$ represents the temperature at which 99% DE is achieved with a residence time of "t" seconds. A table of results from thermal decomposition studies of various hazardous wastes is presented in Table 3. The EPA has funded research in this area and has acquired such a unit at its Hazardous Waste Engineering Research Laboratory in Cincinnati.

Exposure Chamber for Test Methods Development

One of the most important goals for CARB's hazardous waste incineration testing program is the development of a facility for test methods

Table 3. Summary of thermal decomposition data for some organic hazardous wastes (5).

Compound	T _{onset} (°C)	T ₉₉ (°C)	T _{99,99} (°C)	log A (s ⁻¹)	E _a (kcal/mol)	Calculated T ₉₉ (°C)
Acetonitrile	760	900	~950	7.17 ± 4.57	39 ± 23	910
Tetrachloro- ethylene	660	850	920	6.41 ± 0.985	33 ± 5.0	900
Acrylonitrile	650	830	860	6.13 ± 4.31	31 ± 21	910
Methane	660	830	870	9.53 ± 0.531	48 ± 3.0	870
Hexachlorobenzene	650	820	880	8.38 ± 4.59	41 ± 22	850
1,2,3,4- Tetrachlorobenzene	660	800	850	6.28 ± 3.78	30 ± 18	830
Pyridine	620	770	840	5.03 ± 1.57	24 ± 7.0	830
Dichloromethane	650	770	780	12.8 ± 11.3	62 ± 52	810
Carbon Tetrachloride	600	750	820	5.46 ± 0.951	26 ± 4.0	830
Hexachlorobutadiene	620	750	780	12.0 ± 2.87	55 ± 13	770
1,2,4- Trichlorobenzene	640	750	790	8.29 ± 2.85	39 ± 13	790
1,2-Dichlorobenzene	630	740	780	8.65 ± 2.92	40 ± 13	770
Ethane	500	735	785	5.12 ± 1.76	24 ± 8.0	840
Benzene	630	730	760	8.63 ± 1.36	39 ± 6.0	760
Aniline	620	730	750	15.9 ± 4.45	71 ± 19	730
Monochlorobenzene	540	710	780	4.92 ± 3.54	23 ± 15	820
Nitrobenzene	570	670	700	15.1 ± 1.72	64 ± 7.0	670
Hexachloroethane	470	600	640	7.31 ± 1.47	30 ± 6.0	650
Chloroform	410	590	620	12.5 ± 1.97	40 ± 8.0	610
1,1,1- Trichloroethane	390	570	600	8.29 ± 1.02	32 ± 4.0	600

development. It is critical to have confidence in both the sampling methods and the analysis procedures. An experimental exposure chamber has been developed by Battelle's Columbus Laboratories [4] which may have desirable features for CARB's hazardous waste program goals.

The hot gas spiking system developed by Battelle Columbus was designed to test the recovery of low levels of 1,2,3,4-TCDD using both a SASS train and a modified Method 5 train. Analysis of the TCDD recovered was performed by high resolution GC/MS. Thus the goal of this study was to determine the efficiency of collection and retention of low levels of dioxins from combustion effluents.

A pilot plant furnace was used to generate the simulated incinerator flue gas. A low flow rate pump was used to inject a solution containing TCDD into a slip stream of the flue gas where the gas temperature was approximately 260°C. Downstream of the spike injection point, the flue gases were sampled. To prevent emissions of TCDD into the atmosphere, a charcoal canister was used to collect any TCDD that may have escaped the sample trains. A schematic diagram of the system is presented in Figure 5. A summary of the TCDD recoveries from this system is presented in Table 4. These data are provided simply as an indication of the type of information that can be generated using a simulation chamber, such as problems with method recovery efficiency. The recovery efficiencies were fair, varying between 73 to 117% for the SASS train and between 101 to 229% for the MM5 train. The outlying point in the MM5 study would suggest that identification of the source of uncertainty and its correction be undertaken. It would not be possible to obtain this type of information from field data.

A system similar to Battelle Columbus' design could be very useful to CARB. The authors noted that this spiking system could be used to

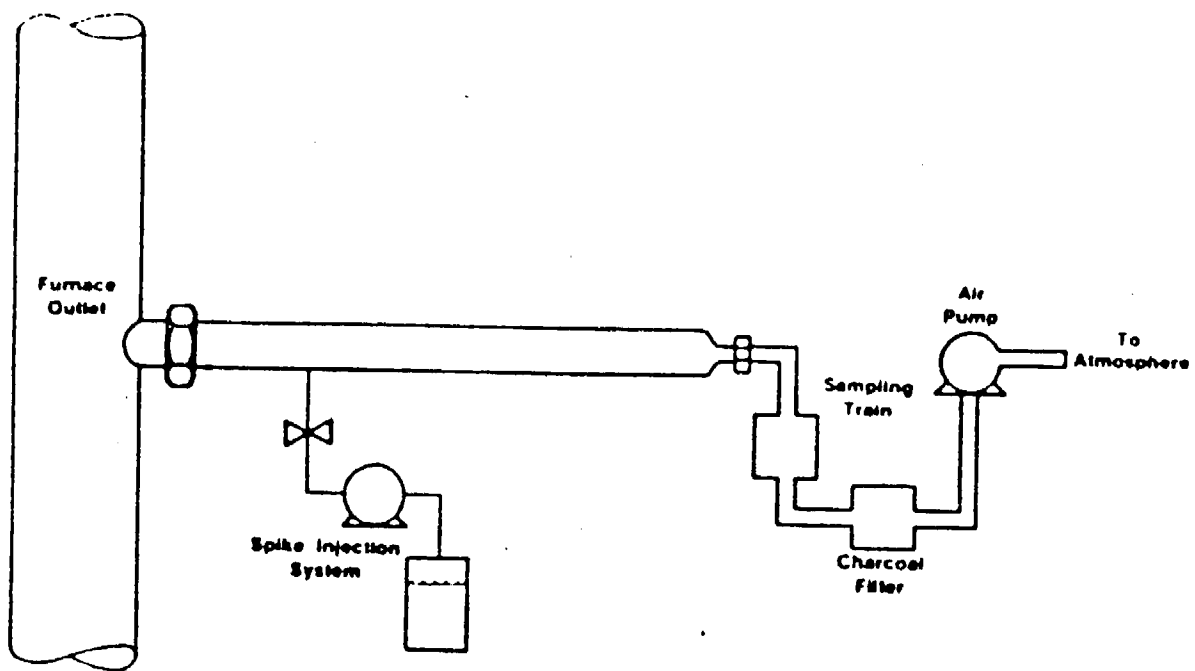


Figure 5. TCDD spike injection and sampling apparatus (4).

Table 4. 1,2,3,4-TCDD recoveries from the hazardous waste spiking system (4).

Test Number	Sampler System	Liquid Spike Volume (mL)	1,2,3,4-TCDD Liquid			Percent Recovery
			Concentration (pg/mL)	Expected Concentration (ng)	Calculated Concentration (ng)	
2 (Dry Air)	SASS	49	500	24	23	94
3	SASS	51	500	25	18	73
4	SASS	42	50	21	17	83
5	SASS	50	5	2.5	2.9	117
6	SASS	51	5	0.25	0.28	113
7	MMS	47	15	7.1	8.0	113
8	MMS	47	12	0.56	0.57	101
9	MMS	49	8	0.39	0.47	120
10	MMS	47	8	0.38	0.87	229

spike a variety of liquid chemicals into a hot flue gas stream for generation of a stream of a known concentration. Such a system could also be used to examine the effects of specific combustion gases and particles on sampling train components (such as the resin trap) and other sources of sampling errors. Based on discussions with Dr. Fred DeRoos at Battelle Columbus, a basic spiking system similar to that described above could be put together for about \$2000 and could be operated and maintained by CARB technicians. Test atmosphere generators for specific compounds are estimated to cost about the same magnitude to construct (about \$2000), and with development costs of about five times that amount (about \$10,000 each).

V. CONCLUSIONS, RECOMMENDATIONS, AND FUTURE RESEARCH NEEDS

The purpose of this study has been to examine research options that CARB can utilize to improve the efficiency and lower the cost of conducting full scale hazardous waste evaluation tests. Specific studies of interest to CARB are:

- 1) development and testing of sampling methods for incineration studies,
- 2) evaluation of the feasibility of using surrogate hazardous waste compounds in incinerator studies, and if feasible, determination of surrogate compounds which best represent complete combustion of the hazardous waste,
- 3) assessment of the influence of incinerator failure conditions on the DRE of hazardous compounds,
- 4) PIC studies and the effect of mixing of fuels on emissions,

- 5) determination of significant operational parameters such as minimum temperature, residence time, oxygen concentration, for effective POHC DE.

Based on the above goals, this feasibility study has discussed what can be accomplished with pilot and laboratory scale studies, the feasibility of renting time on existing pilot scale incinerators, and the feasibility of CARB building and operating its own pilot scale incinerator. Specific conclusions, recommendations, and future research needs are presented below.

Conclusions

The HWI experimental program contemplated by CARB can be developed at the pilot or laboratory scale. A pilot scale program could be developed to model, to some degree, the processes that occur in a full scale combustor. Although quantitative prediction of POHC DE and PIC concentrations is not possible on scaled down versions of full sized HWIs, valuable information can still be obtained from pilot scale studies. It is generally accepted that if quantitative predictions are desired from pilot scale studies, combustion units rated at about 1 MMBtu/hr or larger will do a better job than smaller sized units. To date, pilot scale tests have been conducted to determine flame-mode incinerability rankings, to investigate surrogates as a predictive methodology for POHC DE and PIC emissions, and to determine failure-mode effects on DE and PIC emissions.

The goal of laboratory HWI studies is to isolate and understand one aspect of a given HWI process. The fundamental information obtained from laboratory studies is used to better understand the performance of full scale HWIs. HWI laboratory studies involving combustion of single

droplets, flame-mode kinetic studies, non-flame thermal decomposition studies, and development of a HWI exposure chamber all have merit.

To develop a HWI experimental program at the pilot scale, CARB has a number of options. It may rent time on existing combustion units or construct its own pilot scale combustion facility. To evaluate HWI facilities on which CARB could rent time, a questionnaire was sent to various companies doing HWI research. Information on seven different CUs capable of performing HWI tests was obtained. The data collected and summarized in Table 1, provide a range of incinerator types, sizes, capabilities, and costs. For example, five of the CUs surveyed were liquid injection units, one was a circulating bed unit, and one was a simulated rotary kiln. The range of firing rates burning No. 2 fuel oil, varied between 30 to 2500 KBtu/hr. The rental cost for one week of testing ranged from about \$6000 to \$60,000 per week. With the information provided in Table 1, CARB can evaluate the capabilities and costs of performing pilot scale experiments with a variety of different fuels.

Designs, specifications, and costs for three different HWI pilot scale systems were submitted to evaluate the feasibility of CARB's building and maintaining its own pilot scale combustion facility. Two of the CU designs submitted were liquid injection types and one was a circulating bed type unit. All of the CUs surveyed reported capabilities of burning slurry fuels while one noted the ability of burning chunks of fuel up to 1" in size. The range in costs for turn-key installation was quite large ranging from \$65,000 to \$600,000. The time to complete the design, construction, installation, and shake-down testing varied between 4 and 12 months. The importance of obtaining permits for test burns of HW was also noted in the surveys submitted.

Although a written survey was not conducted to evaluate laboratory

HW combustion units, a brief review of current combustion literature was conducted on single droplet combustion, flame-mode kinetic studies, non-flame thermal decomposition studies, and the development of a HWI exposure chamber.

Single droplet burning studies can provide information on burning and vaporization rates, ignition time delay, droplet extinction, and phenomena associated with "Microexplosions". Utilizing the information generated by research on burning single droplets of HW, an alternative incinerability ranking system might be developed. Because droplet vaporization and burning are central processes in liquid spray combustion systems, an incinerability ranking system based on droplet burning rates may be a method of approaching flame failure modes which would be superior to those previously suggested and which can be used in conjunction with a non-flame incinerability scale such as proposed by Dellinger [5].

Ignition/extinction phenomena, POHC DE, and PIC production are important phenomena in HW combustion that are governed by flame-mode kinetics. Global flame-mode kinetic studies can be conducted by utilizing an opposed-jet diffusion flame burner. However, because of the severe sensitivity of the global rate constant on the kinetic data experimentally generated, sophisticated sampling and analysis techniques must be developed and employed.

Non-flame thermal decomposition studies have been shown to describe POHC destruction in the post-flame region of an incinerator. An experimental apparatus consisting of a thermal decomposition unit and an inline GC has been used to generate thermal decomposition profiles of several different hazardous wastes. Using this information, a non-flame residence time needed to achieve a given DE at a given temperature can

be determined. The EPA has funded such research in the past and has acquired such a unit for its in-house research program.

An experimental exposure chamber has been used for TCDD test method development. A similar apparatus may also prove useful for CARB's methods development. A pilot plant furnace can be used to generate combustion gases and a sample of waste can be injected into a slip-stream of the flue gas, then analyzed. SASS train and MM5 trains have been used to collect TCDD with such a chamber and the data used to demonstrate good overall recoveries reported.

Recommendations

Based on the information presented above and discussions with experts in the field of hazardous waste combustion, the following recommendations are presented.

1. The CARB should not purchase and operate its own pilot scale HWI because of the high initial cost of such a unit, the high level of maintenance and support costs, and the requirement for full-time skilled combustion personnel for generation of combustion data. An initial cost of at least \$65,000 and a period of four months would be needed just to obtain the pilot scale unit. Not included in this estimate are site preparation, analytical equipment, and salary for at least one full time operator (BS level engineer). Although this recommendation eliminates the possibility of CARB operating the CU on its own schedule, the sophisticated and dedicated research effort required for operation of a pilot scale CU may be beyond CARB's capabilities at this time without major resource commitments.
2. To conduct tests on pilot scale incinerators, CARB should consider

contracting for use of pilot scale HWIs owned and operated by private firms engaged in combustion research. Because of the sophisticated nature of combustion testing, the operations of the combustor should be carried out by experienced personnel. On-site tests are sufficiently difficult without the added burden of having to operate the CU. Renting time on existing pilot scale HWIs, as opposed to purchasing and operating a HWI, permits the option of conducting tests on different pilot scale HWI configurations (liquid injection, rotary-kiln, circulating-bed). Because of the companies' previous combustion experience with their CU, the behavior of the CU under standard combustion conditions is probably well known. Thus perturbations from standard conditions due to the combustion of HW and the CU may be more readily recognized. The drawbacks to this recommendation include the need to coordinate a test schedule (several months lead time would normally be required) with many of the logistical problems associated with actual field tests, and the additional costs associated with a test crew leaving the Sacramento area. It should be noted that renting time on a pilot scale CU is not a requisite for many of CARBs test methods development needs (see recommendation #4 below). Pilot scale tests that are feasible for CARB to conduct by renting time on one of the existing pilot scale CU mentioned earlier are:

- 1) to test the effect of various failure conditions on POHC DE and PIC formation for various liquid wastes of interest,
- 2) to determine the effectiveness of microexplosion on reducing POHC penetration and PIC formation,

3) to measure the POHC DE and PIC formation of various solid slurries.

3. Laboratory studies of single droplet combustion and flame-mode chemical kinetics should be pursued. Both of these studies could provide immediate information which may help explain the behavior of HW in full scale incinerators and could be carried out by a contractor or a CARB operated combustion laboratory. Single droplet combustion studies could yield much valuable information relevant to understanding the operation of full scale HWIs. Despite only a modest capital investment (\$10,000), single droplet combustion studies provide information on: a) burning rates of fuel and fuel mixtures, b) ignition and extinction parameters, c) the effect of droplet microexplosion on POHC DE and PIC formation. Extinction studies are particularly relevant to POHC DE and PIC formation studies. At extinction, there is always a finite amount of fuel that escapes the flame environment, which must be destroyed in the relatively cool post-flame zone. Thus sampling of PICs at extinction would complement pilot scale PIC studies as well as the non-flame thermal decomposition studies. Because droplet combustion studies are conducted at the laboratory scale, many fuels and fuel mixtures may be studied relatively easily. In addition, the results from single droplet studies could be used to develop an incinerability ranking scale. Because single droplet combustion involves both transport processes (diffusion) and chemistry (in extinction studies) the single droplet incinerability ranking scale may be an improvement over existing incinerability ranking scales, which for the most part are based only in the chemistry of combustion (e.g.

theoretical flame mode kinetics, non-flame thermal decomposition). Flame-mode combustion studies of HWS would provide details on the flame structures and kinetic pathways of combustion, and could be utilized to conduct detailed PIC studies. Studies involving non-flame thermal decomposition of HW could be coordinated with existing facilities such as the EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati or contracted with a laboratory such as the Dayton Research Institute.

4. For test methods development and practice, an HW exposure chamber should be developed instead of a pilot scale incinerator. Because this is a laboratory scale device, a HW exposure chamber could be installed in existing CARB laboratories or at a rented facility. After having obtained a waste injection system (by contracting out for its development or purchase), the remainder of the system is relatively simple and can be maintained and operated by CARB test engineers and technicians. Specific injection systems for wastes or their flue gas components can be designed and constructed as needed. Such a system could provide information on effects of flue gas composition on sampling efficiency, recovery, precision and accuracy not otherwise available from field tests. Problems could be uncovered before costly tests are undertaken in the field.

Future Research Needs

During the course of this and related studies sponsored by the CARB, we have become aware of several research needs in the field of hazardous waste incineration. Although these were not directly the subject of this report, they are included below for information purposes as CARB's incineration research program is formulated.

1. Almost all of the fundamental research on hazardous waste incineration has been directed toward liquid injection systems thus far. A long term research program on the combustion behavior of slurries and solid wastes should be initiated. Such a program could be started by studying the slurries fed to liquid injection systems. Work in understanding mechanisms involved in municipal solid waste incineration systems (MSWIs) should also be a research priority. Several California Municipalities have either begun construction or have plans on the drawing boards for MSWIs. The recent test series completed by the CARB on pilot and full-scale HWIs indicated low levels of POHC and PIC penetration. We believe that there is evidence in the literature indicating that municipal waste incinerators will have higher total emissions of POHCs and PICs of public concern. The development of solid-phase surrogate "spike" compounds, such as organically treated vermiculite, might be of value in future evaluation of full scale MSWIs, in analogy to the current "spiked soups" used in liquid injection incinerator tests.
2. We believe industry will continue to find alternative methods for recovering energy from more concentrated and higher heating value organic wastes. CARB should probably concentrate its attention on determining the combustion behavior of lower heating value wastes, especially the behavior of aqueous mixtures. We have seen little in the literature to suggest that there is any significant understanding of combustion of this type of waste.

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APPENDIX A

Questionnaire for Evaluation of
Hazardous Waste Incineration Facilities
Available to CARB



COLLEGE OF ENGINEERING
DEPARTMENT OF CIVIL ENGINEERING

DAVIS, CALIFORNIA 95616

Sample of cover letter for the questionnaire.

The California Air Resources Board (CARB) is charged with assisting the Department of Health Services (DOHS) and local air pollution control districts (APCDs) in evaluating applications to burn hazardous wastes in a variety of incinerators. As a result, CARB evaluates a variety of incinerators which burn numerous types of hazardous waste. These evaluation tests typically involve determining the destruction and removal efficiency (DRE) of the incinerator for select compounds, as well as determining the emissions for certain products of incomplete combustion (PIC). Because of the concern about protecting public health from the emission of toxic compounds into the atmosphere, these tests are labor intensive and expensive. A private company can spend \$500,000 for one complete test evaluation. As a result any unanticipated problems at the test site or with the sampling and analytical methods could cause costly delays or require further testing.

To improve the efficiency of conducting these tests and to lower costs, it is desirable to determine and correct any problems with proposed sampling and analytical procedures before CARB site tests are conducted. As a consequence, the CARB would like to develop an experimental program to study hazardous waste incineration. The following goals have been set:

1. To develop and test sampling and collection methods for incineration studies.
2. To perform studies of products of incomplete combustion
3. To study the effect of mixing of fuels on emissions.
4. To evaluate the feasibility of using surrogate hazardous waste compounds in incinerator studies.
5. To study the influence of various "failure conditions" on the DRE of hazardous compounds.
6. To determine the significant operational parameters such as minimum temperature, residence time, oxygen concentration, etc., for effective destruction of hazardous compounds.

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We appreciate your participation in this study. If clarification is required please don't hesitate to contact us.

Sincerely,

Daniel P.Y. Chang
Associate Professor

Nelson W. Sorbo
Research Assistant

DPYC:NWS/gcg

Enclosures

PART I.

CARB's PILOT SCALE HAZARDOUS WASTE INCINERATOR PROGRAM GOALS

CARB would like to obtain a pilot scale incinerator that could be used for combustion evaluation of hazardous wastes. A list of desirable capabilities was provided to us and includes the following:

1. Fuel: The ability to burn gaseous, liquid, or solid fuels. Types of fuels expected to be burned are natural gas, fuel oil, coal, liquid hazardous waste, solid hazardous waste, and reference compounds such as hexachlorobenzene, and sulfur hexafluoride.
2. Fuel handling systems for all of the above.
3. Capability to withdraw at least 10 scfm from the exxhaust stream for exhaust gas analysis equipment.
4. Capability to control residence time and temperature in the combustion zone.
5. Capability to attach control equipment to exhaust stream. Possible control equipment would include scrubbers, baghouse, or an after-burner.
6. Capability of incinerator to destroy hazardous compounds generated by other projects.
7. Use of the incinerator to produce hazardous gas mixtures in a cold gas stream.

The incinerator would be used for the following types of studies:

1. Feasibility of using surrogate compounds for hazardous waste incineration studies.
2. Determining which emission components are the best indicators of complete combustion.
3. Study sampling and collection methods for incineration studies.
4. Study the effect of mixing fuels on emissions.
5. Determination of minimum temperature and residence time for effective destruction of hazardous compounds.
6. Study the effects of various failure conditions on destruction efficiency and products of incomplete combustion.

PART II.

EVALUATION OF EXISTING PILOT SCALE INCINERATOR FACILITIES FOR HAZARDOUS WASTE INCINERATION TRIAL BURNS BY CARB

The purpose of this part of the evaluation is to give CARB an idea as to the range of incineration studies which could be carried out by renting time on existing pilot scale incinerators. To describe the capabilities and features of your pilot scale incinerator(s) that may be used by CARB for hazardous waste incineration tests, please complete the following questionnaire with short answers. If the categories given do not accurately or completely describe the capabilities of your facility, please add the appropriate information. Please respond to these questions based on the ability of your facilities to meet CARB's goals stated in Part I. If your company has multiple systems which CARB may utilize, please complete a questionnaire for each system using the enclosed additional pages.

The questionnaire should be answered based on the following scenario:

CARB will provide all technical personnel and analytical support related to sampling, i.e., all sampling instruments and analysis of all sample data. The contracting company will provide: use of a combustion unit for one week with all personnel necessary for its operation, a fuel specified by CARB, all data dealing with the operation of the combustion unit (i.e., fuel rate, air rate, temperatures, flame temperature, burner settings, etc.), necessary approvals from local agencies to conduct the test burns.

PART II. - QUESTIONNAIRE

Name of Company

Name of Combustion Unit

1. Range of firing rates of the pilot scale combustion unit (CU) for a nominal No. 2 fuel oil.
2. Corresponding approximate exhaust gas flowrate.
3. For liquid fuels, what is the range of fuel viscosities that can be fired?
4. Can a tracer gas such as SF₆ be continuously injected into the liquid fuel stream (approximately 0.2 ml SF₆ per liter of fuel)? If SF₆ cannot be injected into the liquid fuel stream directly, are there possibilities of injection near the burner?
5. Are ports available for flame temperature determination using optical pyrometry? suction pyrometry? Do you routinely measure the flame temperature in the CU? What technique is used?

6. Can flame impingement on a cold surface be simulated? Please describe. Can a cold wall quench be simulated? If so, please describe the placement of the quenching wall and how the cold wall is cooled?
7. Can the injection of the combustion air be staged for this CU? Please describe.
8. What is the range of swirl numbers available on the CU burner for combustion of a nominal No. 2 fuel oil?
9. Could a failure of the CU burner atomizer be simulated? Please describe.
10. Can the temperature history of the gases in the post flame region be obtained?

11. Is wall temperature data available.?
12. Is it possible to change the volume of the CU by bolting on another section? How long would it take to change the CU volume? By what percentage can the original volume of the CU be changed by the bolt-on section(s).
13. How many ports are available for sampling along the post flame region?
14. Please describe data gathering/analysis capabilities that are available for CU tests (real time temperatures/flow/gas concentration information, computer plots, statistical information, etc.).
15. Is there a computer model for this CU available? What parameters can be modeled?
16. Are burners that simultaneously inject both liquid waste and gaseous fuels available for the CU?

17. Is a gas burner available for the CU?
18. The following relate to combustion of solids in the CU. For this CU, are burners available for combustion of liquid slurries containing solids, e.g., can the EPA soups containing kitty litter be combusted? What solids and liquids have been tested? What is the maximum permissible size of solids?

19. Please estimate the cost charged to CARB to run a test for one week (Monday to Friday). Assume: a) a practice run on Monday afternoon, 4 days of tests, b) one contractor supplied liquid fuel (specified by CARB) will be used during the entire week, c) the following failure conditions will be simulated (if possible): atomizer failure, wall or flame impingement quench, high excess air, low excess air, d) SF6 injection will be performed during all tests, (CARB will supply all personnel for analysis and monitoring of SF6 test, contractor will provide an injection port into fuel line), e) contracting company must provide: the use of a CU with all necessary personnel for its operation, all process information (rates, temperatures, flame temperatures, concentrations, etc.), and access to CARB for a stack test. Assume that CARB will gather samples during regular working hours only.

PART III.

CARB PILOT SCALE INCINERATOR

CARB would like to obtain a small scale combustion unit (CU) that can be used for evaluation of hazardous waste combustion. The CU should have the following capabilities:

1. Nominally rated at 70 to 150 kBTU/hr for a No. 2 fuel oil.
2. Burner with the following capabilities:
 - a. to burn liquid fuels within a range of viscosities (No. 2 fuel oil to toluene)
 - b. to burn slurry fuels
 - c. to allow for variation of swirl number
3. CU design to allow for testing of the following failure conditions: low excess air, high excess air, wall quench, atomizer failure.
4. Modular design so that the combustion volume can be changed by bolting on another section.
5. All controls and appurtences necessary for operation and monitoring (including burner with controls, compressors, gauges, fuel monitoring controls, furnace shell with ports for samples, thermocouples for wall and combustion product temperature profiles, port for flame temperature measurement) except for gas analysis and data acquisition equipment.
6. A port for the injection of SF₆ into the fuel stream.
7. An afterburner section downstream of the final sample port. This is needed to assure complete destruction of all hazardous products present in the combustion gases, independent of the operation of the CU.
8. "Turn-key" installation.
9. Operator training.

Based on the criteria presented above, summarize in a general way the CU that you can provide that can meet most of CARB's desires. Please include an estimate of the uncertainty of the cost estimate. Also include an estimate of the delivery time for design, construction, installation, and shake-down testing.

APPENDIX B

Responses to Part II of Questionnaire:
Evaluation of Existing Pilot Scale Incinerators
for Hazardous Waste Incineration Trial Burns by CARB

PART II. - QUESTIONNAIRE

Name of Company

Name of Combustion Unit

CU-A

1. Range of firing rates of the pilot scale combustion unit (CU) for a nominal No. 2 fuel oil.

250,000 - 2,000,000 Btu/hr

2. Corresponding approximate exhaust gas flowrate.

50 - 350 SCFM

3. For liquid fuels, what is the range of fuel viscosities that can be fired?

From very thin solvents to thick viscous sludges

4. Can a tracer gas such as SF₆ be continuously injected into the liquid fuel stream (approximately 0.2 ml SF₆ per liter of fuel)? If SF₆ cannot be injected into the liquid fuel stream directly, are there possibilities of injection near the burner?

Yes - either into the liquid or into the burner.

5. Are ports available for flame temperature determination using optical pyrometry? suction pyrometry? Do you routinely measure the flame temperature in the CU? What technique is used?

Temperatures are extremely uniform and are normally maintained in the range of 1400°F-1800°F.

Precise measurement is accomplished using Type K thermocouples at over 20 elevations. There is no flame so flame pyrometry is not needed.

6. Can flame impingement on a cold surface be simulated? Please describe. Can a cold wall quench be simulated? If so, please describe the placement of the quenching wall and how the cold wall is cooled?

Bayonet coolers are inserted into the combustion chamber to remove heat of combustion. They operate below 150°F, thus giving a cold wall surface. Please note that the high degree of turbulent mixing in a circulating bed eliminates the effects of a cold surface.

7. Can the injection of the combustion air be staged for this CU? Please describe.

Five levels of staged combustion air are installed and can be modulated during tests to optimize emissions.

8. What is the range of swirl numbers available on the CU burner for combustion of a nominal No. 2 fuel oil?

No swirl - liquid fuels are fed through an open pipe.

9. Could a failure of the CU burner atomizer be simulated? Please describe.

The unit is operated without any atomizers, even with liquids of a wide variety of viscosities. The high degree of turbulent mixing eliminates any requirement for an atomizer.

10. Can the temperature history of the gases in the post flame region be obtained?

There are 20 temperature measurements between the combustor and the exhaust stack.

11. Is wall temperature data available.? Yes - the refractory walls and the outer metal shell are well instrumented.

12. Is it possible to change the volume of the CU by bolting on another section? How long would it take to change the CU volume? By what percentage can the original volume of the CU be changed by the bolt-on section(s).

Yes, it would take a few days to add or subtract combustion chamber spool pieces. Each one adds or subtracts 1/2 second of residence time.

13. How many ports are available for sampling along the post flame region?

5-10 with a minimum of adaptation.

14. Please describe data gathering/analysis capabilities that are available for CU tests (real time temperatures/flow/gas concentration information, computer plots, statistical information, etc.).

A full range of temperatures, flow rates, pressures, and flue gas compositions are monitored and displayed on a real time basis. All data is also routed to a continuous data logger and is computer plotted and manipulated for correlations after the test.

15. Is there a computer model for this CU available? What parameters can be modeled? The incinerator operates at such extremely even temperatures and with such high turbulence that the performance reduces to simple oxidation kinetics. Other incinerators require numerical models to account for wide swings in temperature and lack of proper mixing. Regression analysis of data correlations by UC-Davis have verified these facts in finding that data from circulating bed incinerators has a remarkably high level of correlation.

16. Are burners that simultaneously inject both liquid waste and gaseous fuels available for the CU?

This is done routinely.

17. Is a gas burner available for the CU?

Yes.

18. The following relate to combustion of solids in the CU. For this CU, are burners available for combustion of liquid slurries containing solids, e.g., can the EPA soups containing kitty litter be combusted? What solids and liquids have been tested? What is the maximum permissible size of solids?

Solids up to 1" are routinely processed. Slurries are also routinely processed. A partial list of materials previously tested is attached.

19. Please estimate the cost charged to CARB to run a test for one week (Monday to Friday). Assume: a) a practice run on Monday afternoon, 4 days of tests, b) one contractor supplied liquid fuel (specified by CARB) will be used during the entire week, c) the following failure conditions will be simulated (if possible): atomizer failure, wall or flame impingement quench, high excess air, low excess air, d) SF6 injection will be performed during all tests, (CARB will supply all personnel for analysis and monitoring of SF6 test, contractor will provide an injection port into fuel line), e) contracting company must provide: the use of a CU with all necessary personnel for its operation, all process information (rates, temperatures, flame temperatures, concentrations, etc.), and access to CARB for a stack test. Assume that CARB will gather samples during regular working hours only.

~ \$60,000

Please note: that the possession of US-EPA permits is a crucial factor in your evaluation. The facility selected should have already submitted and be at least close to receiving permission for a trial burn for RCRA (hazardous) and TSCA (toxic) type wastes, otherwise it is unlikely that waivers from US-EPA or CAL-DHS will be granted - even for government sponsored research.

GA plans for their RCRA and TSCA trial burns to be done in April and May of 1985.

PART II. - QUESTIONNAIRE

NAME OF COMPANY

NAME OF COMBUSTION UNIT

CU-B

1. RANGE OF FIRING RATES OF THE PILOT SCALE COMBUSTION UNIT (CU) FOR A NOMINAL NO. 2 FUEL OIL.

.8 - 2.5 Million Btu/Hr

2. CORRESPONDING APPROXIMATE EXHAUST GAS FLOWRATE.

150 - 550 SCFM (depends on excess air; exhaust gas flowrate is about 165 SCFM per 10^6 Btu/hr heat input at 0% exhaust O_2 for No 2 fuel oil)

3. FOR LIQUID FUELS, WHAT IS THE RANGE OF FUEL VISCOSITIES THAT CAN BE FIRED?

30 - 900 SSU @ 100°F. The heavier fuel oil must be heated to achieve a fuel viscosity in the range of 30 to 100 SSU. The facility has the equipment to heat these fuels.

4. CAN A TRACER GAS SUCH AS SF6 BE CONTINUOUSLY INJECTED INTO THE LIQUID FUEL STREAM (APPROXIMATELY 0.2 ML SF6 PER LITER OF FUEL)? IF SF6 CANNOT BE INJECTED INTO THE LIQUID STREAM DIRECTLY, ARE THERE POSSIBILITIES OF INJECTION NEAR THE BURNER?

Injection either into the fuel oil line or near the burner is possible. Alternatively an air or steam atomized nozzle can be used and the SF6 injected into this gas stream. Another approach would be to use a dual fuel nozzle and inject the SF6 into the gas nozzle when firing on liquid fuels.

5. ARE PORTS AVAILABLE FOR FLAME TEMPERATURE DETERMINATION USING OPTICAL PYROMETRY? SUCTION PYROMETRY? DO YOU ROUTINELY MEASURE THE FLAME TEMPERATURE IN THE CU? WHAT TECHNIQUE IS USED?

Eight 3" diameter ports and sixteen 1" diameter ports are spaced along the length of the furnace on each of the side walls. Eight ports are spaced along the top wall as illustrated in the attached brochure. These can also be used for optical or suction pyrometry. Both bare Pt-Pt/Rd (Type R)

thermocouples and suction pyrometers are routinely utilized in the facility. When no cooling surface is installed in the unit bare thermocouples yield results very close to suction pyrometry.

6. CAN FLAME IMPINGEMENT ON A COLD SURFACE BE SIMULATED? PLEASE DESCRIBE. CAN A COLD WALL QUENCH BE SIMULATED? IF SO, PLEASE DESCRIBE THE PLACEMENT OF THE QUENCHING WALL AND HOW THE COLD WALL IS COOLED.

Yes to both. Either water cooled or Therminol (100-500°F) cooled panels have been utilized in the CU. These panels may be fabricated with any surface area depending on the requirement of the experiment and placed at any position within the 33" diameter firebox. Generally a serpentine pattern for the cooling path is chosen. The coolant enters and exits through two or more of the numerous ports located along the length of the CU. Flame impingement is simulated by placing the panel such that the flame can strike the surface. Varying degrees of impingement can also be achieved by changing the flame shape through swirl or nozzle style.

7. CAN THE INJECTION OF THE COMBUSTION AIR BE STAGED FOR THIS CU? PLEASE DESCRIBE.

Yes. Again the numerous ports can be used to inject staging air into the CU. A movable manifold allows staged air to be injected at any axial location along the CU. A separate valve and orifice are used to control and measure the staged air addition rate. This air is currently fed using the burner air forced draft fan so it will have the same temperature as the main combustion air. Preheat is possible to about 600°F.

8. WHAT IS THE RANGE OF SWIRL NUMBERS AVAILABLE ON THE CU BURNER FOR COMBUSTION OF A NOMINAL NO. 2 FUEL OIL?

An IFRF Type Variable Swirl Block Burner is used on this facility. Swirl numbers as calculated by Beer & Chigier (Combustion Thermodynamics) from 0 to 0.85 can be achieved.

9. COULD A FAILURE OF THE CU BURNER ATOMIZER BE SIMULATED? PLEASE DESCRIBE.

If an air or steam atomized nozzle is utilized the easiest way to simulate a failed nozzle is to reduce or turn off the atomized air. With a pressure atomized nozzle an oversized nozzle could be used to produce large fuel droplets. Alternatively no nozzle or a rotating disk burner could be utilized.

10. CAN THE TEMPERATURE HISTORY OF THE GASES IN THE POST FLAME REGION BE OBTAINED?

Yes; again access ports are available over the whole length of the combustor and into the convection passages. Thermocouples or a suction pyrometer can be used at any of these ports to obtain both radial and axial temperature

11. IS WALL TEMPERATURE DATA AVAILABLE?

Yes, there are type K thermocouples embedded in the walls 1" below the surface near the flame regions.

12. IS IT POSSIBLE TO CHANGE THE VOLUME OF THE CU BY BOLTING ON ANOTHER SECTION? HOW LONG WOULD IT TAKE TO CHANGE THE CU VOLUME? BY WHAT PERCENTAGE CAN THE ORIGINAL VOLUME OF THE CU BE CHANGED BY THE BOLT-ON SECTION(S).

The facility is designed in sections to enable changes in combustion volume. It would take approximately 1 week to change this volume. Alternatively sampling could be made along the length of the CU. The CU is made up of two 3' sections and two 2' sections. So the combustion volume can be changed by about a factor of 5.

13. HOW MANY PORTS ARE AVAILABLE FOR SAMPLING ALONG THE POST FLAME REGION?

There are 24 ports along each side of the furnace for a total of 48. In addition there are 8 ports on the top and a 10" X 10" refractory plug in the 2' section.

14. PLEASE DESCRIBE DATA GATHERING/ANALYSIS CAPABILITIES THAT ARE AVAILABLE FOR CU TESTS (REAL TIME TEMPERATURES/FLOW/GAS CONCENTRATION INFORMATION, COMPUTER PLOTS, STATISTICAL INFORMATION, ETC.).

Temperatures are monitored at a central thermocouple readout. The main combustion air flow is monitored by a hot wire type mass flow meter; staged air and atomization air or steam is measured using orifices. Continuous sampling for O_2 , CO_2 , CO, NO_x , SO_2 , and TUHC (with an appropriate gas conditioning system) are also available. Particulate sampling, modified Method 5 for semivolatile organics and VOST trains for volatile organics are also available. All data are collected manually except for continuous strip charts of the emissions. Data loggers are also available for extended tests. Apple Computers are available for data analysis and plotting.

15. IS THERE A COMPUTER MODEL FOR THIS CU AVAILABLE? WHAT PARAMETERS CAN BE MODELED?

Yes. This is primarily a heat transfer model of the combustor to predict temperature profiles as a function of firing rate, excess air, fuels, and cooling surface available. Equilibrium combustion codes are also used to predict specie concentrations as a function of temperature & fuel composition. Kinetic codes are available to predict gaseous specie concentration as a function of time.

16. ARE BURNERS THAT SIMULTANEOUSLY INJECT BOTH LIQUID WASTE AND GASEOUS FUELS AVAILABLE FOR THE CU?

Dual fuel nozzles have been routinely employed in the IFRF Burner.

17. IS A GAS BURNER AVAILABLE FOR THE CU?

Yes

18. THE FOLLOWING RELATE TO COMBUSTION OF SOLIDS IN THE CU. FOR THIS CU, ARE BURNERS AVAILABLE FOR COMBUSTION OF LIQUID SLURRIES CONTAINING SOLIDS, E.G., CAN THE EPA SOUP CONTAINING KITTY LITTER BE COMBUSTED? WHAT SOLIDS AND LIQUIDS HAVE BEEN TESTED? WHAT IS THE MAXIMUM PERMISSIBLE SIZE OF SOLIDS?

Solids containing slurries can be handled as long as the maximum particle size does not exceed the minimum orifice size in either the nozzle or fuel delivery system. For pressure atomized nozzles this is limited to about 100 μ m. Larger particles can be accommodated with air atomized nozzles but is dependent on the nozzle design. The resulting viscosity of the slurry must also be evaluated to insure pumpability. It may be necessary to pulverize large solids. Alternatively special slurry handling systems could be developed and fabricated. However, because of the horizontal orientations and low velocity of the combustion products the maximum particle size that can be injected into the facility without it falling to the bottom is limited to about 200 μ m. Coal-oil mixtures, of up to 50% solids have been fired in this unit and a special slurry fuel handling system was developed for these tests. The solids, however, were pulverized to 70% through 200 mesh prior to mixing with the oil. With this particle size and solids concentration, severe nozzle erosion and pump performance problems were encountered.

Of course pulverized coal which is pneumatically transported to the burner is routinely fired in this unit. Again the coal grind is a standard utility grind of 70% through 200 mesh.

Both solid and liquid forms of solvent refined coal were test fired in this facility. Special water cooled nozzles were required to handle solid SRC to prevent melting and coking. Some of the liquid forms required preheating to ensure good atomization. Other liquids fired in this CU include No. 2 fuel oil mixed with various hazardous compounds, such as chlorobenzene, carbon tetrachloride, chloroform, methylene chloride and dichloroethane with the hazardous compounds not exceeding 10%. The purpose of these studies was to study the thermal destruction of chlorinated wastes by cofiring with conventional fuels. A synthetic waste consisting of 70% methanol, 20% water, and 5% each of methylene chloride, chloroform and chlorobenzene was also tested in a study of various surrogates for DRE.

19. PLEASE ESTIMATE THE COST CHARGED TO CARB TO RUN A TEST FOR ONE WEEK (MONDAY TO FRIDAY). ASSUME: a) A PRACTICE RUN ON MONDAY AFTERNOON, 4 DAYS A TEST, b) ONE CONTRACTOR SUPPLIED LIQUID FUEL (SPECIFIED BY CARB) WILL BE USED DURING THE ENTIRE WEEK, c) THE FOLLOWING FAILURE CONDITIONS WILL BE SIMULATED (IF POSSIBLE): ATOMIZER FAILURE, WALL OR FLAME IMPINGEMENT QUENCH, HIGH EXCESS AIR, LOW EXCESS AIR, d) SF6 INJECTION WILL BE PERFORMED DURING ALL TESTS, (CARB WILL SUPPLY ALL PERSONNEL FOR ANALYSIS AND MONITORING OF SF6 TEST, CONTRACTOR WILL PROVIDE AN INJECTION PORT INTO FUEL LINE), e) CONTRACTING COMPANY MUST PROVIDE: THE USE OF A CU WITH ALL NECESSARY PERSONNEL FOR ITS OPERATION, ALL PROCESS INFORMATION (RATES, TEMPERATURES, FLAME TEMPERATURES, CONCENTRATIONS, ETC.), AND ACCESS TO CARB FOR STACK TEST. ASSUME THAT CARB WILL GATHER SAMPLES DURING REGULAR WORKING HOURS ONLY.

One week (5 working days) of testing will cost \$10,500. This includes one full time test engineer, one full time and one half time facility technician, one half-time facility supervising engineer, equipment use fees, and fuel.

This cost does not include expenditures for facility set-up and preparation (e.g. installation of waterwall panels, placement of staged air manifold, procuring test equipment and fuel, developing a test plan). These costs are very project specific, but are generally at least as much as that noted above for actual testing.

Post test costs (data reporting, returning the facility to an appropriate base configuration, etc.) are also not included in the above, and can be as much as a single week of testing.

PART II. - QUESTIONNAIRE

NAME OF COMPANY -

NAME OF COMBUSTION UNIT - CU-C

1. RANGE OF FIRING RATES OF THE PILOT SCALE COMBUSTION UNIT (CU) FOR A NOMINAL NO. 2 FUEL OIL.

30 - 100,000 Btu/Hr

2. CORRESPONDING APPROXIMATE EXHAUST GAS FLOWRATE.

6 - 30 SCFM (depending on excess air; exhaust gas flowrate is about 16.5 SCFM at 0% percent exhaust O₂ per 100,000 Btu/Hr heat input for No. 2 fuel oil).

3. FOR LIQUID FUELS, WHAT IS THE RANGE OF FUEL VISCOSITIES THAT CAN BE FIRED?

30 - 900 SSU @ 100°F. The heavier fuel oil must be heated to achieve a fuel viscosity in the range of 30 - 100 SSU. The facility has the equipment to heat these fuels.

4. CAN A TRACER GAS SUCH AS SF₆ BE CONTINUOUSLY INJECTED INTO THE LIQUID FUEL STREAM (APPROXIMATELY 0.2 ML SF₆ PER LITER OF FUEL)? IF SF₆ CANNOT BE INJECTED INTO THE LIQUID STREAM DIRECTLY, ARE THERE POSSIBILITIES OF INJECTION NEAR THE BURNER?

Injection into the fuel oil line or one of the air streams is possible. An air or steam atomized nozzle can also be used and the SF₆ injected into the atomizing gas. Alternatively a dual fuel nozzle can be used and the SF₆ can be injected into the gas nozzle when firing on liquid fuels.

5. ARE PORTS AVAILABLE FOR FLAME TEMPERATURE DETERMINATION USING OPTICAL PYROMETRY? SUCTION PYROMETRY? DO YOU ROUTINELY MEASURE THE FLAME TEMPERATURE IN THE CU? WHAT TECHNIQUE IS USED?

Ports are available over the whole length of the 8" diameter combustion chamber for temperature measurements or sampling. Although bare (type R, (Pt/Pt/Rd)) thermocouples are routinely used for temperature measurement, an optical or suction pyrometer could be used in the 1-1/2" diameter access ports. With other combustion apparatus it has been found that bare thermocouples yield results very close to a

suction pyrometer when there is a hot refractory wall.

6. CAN FLAME IMPINGEMENT ON A COLD SURFACE BE SIMULATED? PLEASE DESCRIBE. CAN A COLD WALL QUENCH BE SIMULATED? IF SO, PLEASE DESCRIBE THE PLACEMENT OF THE QUENCHING WALL AND HOW THE COLD WALL IS COOLED.

Yes, flame impingement on a cold surface can be simulated. Water cooled tubes can be inserted in any of the 38 access ports or a water cooled sleeve could be inserted into the 8" diameter combustion chamber. The cooled tubes can be set either perpendicular or parallel to the main flow. A closed loop Therminol system (100-500°F) for these cooling surfaces could be assembled as well.

7. CAN THE INJECTION OF THE COMBUSTION AIR BE STAGED FOR THIS CU? PLEASE DESCRIBE.

Staged air can be injected into any of the 38 access ports located along the length of the CU. Separate control and measurement of these flows is possible. Different mixing techniques are also possible.

8. WHAT IS THE RANGE OF SWIRL NUMBERS AVAILABLE ON THE CU BURNER FOR COMBUSTION OF A NOMINAL NO. 2 FUEL OIL?

A subscale dual register burner is normally used on this facility. Therefore there are two concentric air passages with independent control of swirl. The inner passage can vary the swirl number from 0 to 22. The outer swirl number can be varied from 0 to 0.4 (Beer and Chigier, Combustion Thermodynamics).

9. COULD A FAILURE OF THE CU BURNER ATOMIZER BE SIMULATED? PLEASE DESCRIBE.

If an air or steam atomized nozzle is used the failure can be simulated by reducing or turning off the atomization fluid. If the nozzle is a pressure atomized nozzle an oversized nozzle could be used.

10. CAN THE TEMPERATURE HISTORY OF THE GASES IN THE POST FLAME REGION BE OBTAINED?

Yes ports are available along the entire length of the combustion chamber. However, it should be noted that this facility is designed to study the first 1-1/2 seconds of combustion residence time.

11. IS WALL TEMPERATURE DATA AVAILABLE?

Thermocouples can be embedded in refractory plugs to be inserted into the access ports. Currently there are no embedded wall thermocouples.

12. IS IT POSSIBLE TO CHANGE THE VOLUME OF THE CU BY BOLTING ON ANOTHER SECTION? HOW LONG WOULD IT TAKE TO CHANGE THE CU VOLUME? BY WHAT PERCENTAGE CAN THE ORIGINAL VOLUME OF THE CU BE CHANGED BY THE BOLT-ON SECTION(S).

Theoretically, the combustions volume could be changed. However, considerable modifications to the facility would be required making it impractical to do so. Alternatively sampling could be done within the combustion volume at locations that represent various residence times. Residence times from a few milliseconds to about 1 second can be accommodated.

13. HOW MANY PORTS ARE AVAILABLE FOR SAMPLING ALONG THE POST FLAME REGION?

There are 38 1-1/2" diameter ports spaced at 90° intervals along every 6 inches of the combustor.

14. PLEASE DESCRIBE DATA GATHERING/ANALYSIS CAPABILITIES THAT ARE AVAILABLE FOR CU TESTS (REAL TIME TEMPERATURES/FLOW/GAS CONCENTRATION INFORMATION, COMPUTER PLOTS, STATISTICAL INFORMATION, ETC.).

All temperatures are monitored on a central digital read-out with manual recording. Flows are measured with rotameter and also recorded manually. Continuous measurement of O₂, CO₂, CO, NO_x, SO₂ and TUHC is available and monitored on strip chart recorders. Apple Computers are available for data analysis and plotting.

15. IS THERE A COMPUTER MODEL FOR THIS CU AVAILABLE? WHAT PARAMETERS CAN BE MODELED?

Equilibrium and kinetic combustion codes are available to predict gaseous specie concentrations as a function of time.

16. ARE BURNERS THAT SIMULTANEOUSLY INJECT BOTH LIQUID WASTE AND GASEOUS FUELS AVAILABLE FOR THE CU?

Dual fuel nozzles are easily employed in the dual register burner.

17. IS A GAS BURNER AVAILABLE FOR THE CU?

Yes

18. THE FOLLOWING RELATE TO COMBUSTION OF SOLIDS IN THE CU. FOR THIS CU, ARE BURNERS AVAILABLE FOR COMBUSTION OF LIQUID SLURRIES CONTAINING SOLIDS, E.G., CAN THE EPA SOUP CONTAINING KITTY LITTER BE COMBUSTED? WHAT SOLIDS AND LIQUIDS HAVE BEEN TESTED? WHAT IS THE MAXIMUM PERMISSIBLE SIZE OF SOLIDS?

Solids containing slurries can be handled as long as the maximum particle size does not exceed the minimum opening size in either the nozzle or fuel delivery system. The resulting viscosity of the slurry must also be evaluated to insure pumpability. It may be necessary to pulverize any large solids. Alternatively special slurry handling systems could be developed and built. The conventional pressure atomized nozzle in this size range cannot tolerate particles greater than about 100µm. Air atomized nozzles could tolerate much larger particles. Because the unit is vertically down fired most any particle size that can be successfully passed through an atomized nozzle can be tolerated in the furnace. However, if there are significant quantities of large ash particles, provision may have to be made for continuous removal of the bottom ash. Other liquid compounds which have been fired in this CU include heavy fuel oil, and various liquid forms of solvent refined coal.

19. PLEASE ESTIMATE THE COST CHARGED TO CARB TO RUN A TEST FOR ONE WEEK (MONDAY TO FRIDAY). ASSUME: a) A PRACTICE RUN ON MONDAY AFTERNOON, 4 DAYS TESTS, b) ONE CONTRACTOR SUPPLIED LIQUID FUEL (SPECIFIED BY CARB) WILL BE USED DURING THE ENTIRE WEEK, c) THE FOLLOWING FAILURE CONDITIONS WILL BE SIMULATED (IF POSSIBLE): ATOMIZER FAILURE, WALL OR FLAME IMPINGEMENT QUENCH, HIGH EXCESS AIR, LOW EXCESS AIR, d) SF6 INJECTION WILL BE PERFORMED DURING ALL TESTS, (CARB WILL SUPPLY ALL PERSONNEL FOR ANALYSIS AND MONITORING OF SF6 TEST, CONTRACTOR WILL PROVIDE AN INJECTION PORT INTO FUEL LINE), e) CONTRACTING COMPANY MUST PROVIDE: THE USE OF A CU WITH ALL NECESSARY PERSONNEL FOR ITS OPERATION, ALL PROCESS INFORMATION (RATES, TEMPERATURES, FLAME TEMPERATURES, CONCENTRATIONS, ETC.), AND ACCESS TO CARB FOR A STACK TEST. ASSUME THAT CARB WILL GATHER SAMPLES DURING REGULAR WORKING HOURS ONLY.

One week (5 working days) of testing will cost \$6500.00. This includes one half-time test engineer, one full-time test technician, appropriate supervising engineering effort, equipment use fee, and fuel.

This cost does not include expenditure for facility setup and preparation (e.g. installation of quenching surfaces, placement of staged air manifold, procuring test equipment and fuel, developing a test plan). These costs are very project specific but are generally at least as much as that noted above for actual testing.

Post test costs (data reporting, returning the facility to an appropriate base configuration, etc.) are also not included in the above, and can be as much as a single week of testing.

PART II. - QUESTIONNAIRE

Name of Company

Name of Combustion Unit

CU-D

1. Range of firing rates of the pilot scale combustion unit (CU) for a nominal No. 2 fuel oil.

40-150 kBtu/hr

2. Corresponding approximate exhaust gas flowrate.

1-40 scfm (wet basis).

3. For liquid fuels, what is the range of fuel viscosities that can be fired?

- No lower limit
- Upper limit: 200 SSU (\cong 43 cS). Limited by atomization, however fuel may be heated to attain this viscosity.

4. Can a tracer gas such as SF₆ be continuously injected into the liquid fuel stream (approximately 0.2 ml SF₆ per liter of fuel)? If SF₆ cannot be injected into the liquid fuel stream directly, are there possibilities of injection near the burner?

SF₆ is a gas, and cannot be added to the liquid fuel without disrupting the performance of pressure jet atomizers. It would cause intermittent sputtering from the nozzle. It could be used in the air side of a twin-fluid atomizer or separately injected at the nozzle tip.

5. Are ports available for flame temperature determination using optical pyrometry? suction pyrometry? Do you routinely measure the flame temperature in the CU? What technique is used?

Flame temperature access ports are available. We generally use suction pyrometry for routine measurements in bench-scale flames.

6. Can flame impingement on a cold surface be simulated? Please describe. Can a cold wall quench be simulated? If so, please describe the placement of the quenching wall and how the cold wall is cooled?

Flame impingement: This has been simulated by placing a water-cooled spiral coil directly into the flame zone. The impingement of the flame onto the cold surface produces marked quench behavior.

Cold walls: These are simulated by use of double jacketed stainless steel water-cooled walls. Cooling water is circulated in the gap between the inner and outside wall.

7. Can the injection of the combustion air be staged for this CU? Please describe.

No. This unit was designed to represent primary flame zone behavior; post flame processes such as air staging were not designed into the present system.

8. What is the range of swirl numbers available on the CU burner for combustion of a nominal No. 2 fuel oil?

Zero to 2.4

9. Could a failure of the CU burner atomizer be simulated? Please describe.

Yes. The pressure jet nozzle has been replaced by one with a higher capacity to simulate atomizer failure. At constant fuel flow this yields the larger droplets and low fuel pressure drop characteristic of worn or failed atomizers. A Malvern laser diffraction particle size analyzer can be used to directly determine the atomization quality.

10. Can the temperature history of the gases in the post flame region be obtained?

Yes. Suction pyrometry will yield the post-flame thermal field.

11. Is wall temperature data available.? Yes

12. Is it possible to change the volume of the CU by bolting on another section? How long would it take to change the CU volume? By what percentage can the original volume of the CU be changed by the bolt-on section(s).

Yes. Reactor is made up of three 0.8 cubic foot sections. Configuration of 0.8, 1.6, and 2.4 cubic feet are possible. These can be interchanged within one hour.

13. How many ports are available for sampling along the post flame region?

One port is available at the reactor exit.

14. Please describe data gathering/analysis capabilities that are available for CU tests (real time temperatures/flow/gas concentration information, computer plots, statistical information, etc.).

Reactor flows:

- Air: venturi
- Fuel: rotameter

Temperature:

- Exhaust gas: thermocouple

Composition of exhaust gas

- CO: Anarad NDIR
- CO₂: Beckman NDIR

- O₂: Taylor paramagnetic
- Total hydrocarbons: Beckman 402 Flame Ionization Detector

15. Is there a computer model for this CU available? What parameters can be modeled? Yes. A two-dimensional model of the TFR can be configured from Richter's Monte Carlo radiation heat transfer model. This thermal information can be coupled into a waste DRE code that uses the various thermal pathways through the reactor to calculate an overall DRE.

16. Are burners that simultaneously inject both liquid waste and gaseous fuels available for the CU?

Not presently. These could be fabricated with little difficulty.

17. Is a gas burner available for the CU?

Yes.

18. The following relate to combustion of solids in the CU. For this CU, are burners available for combustion of liquid slurries containing solids, e.g., can the EPA soups containing kitty litter be combusted? What solids and liquids have been tested? What is the maximum permissible size of solids?

No solids or slurries have been tested in this unit.

19. Please estimate the cost charged to CARB to run a test for one week (Monday to Friday). Assume: a) a practice run on Monday afternoon, 4 days of tests, b) one contractor supplied liquid fuel (specified by CARB) will be used during the entire week, c) the following failure conditions will be simulated (if possible): atomizer failure, wall or flame impingement quench, high excess air, low excess air, d) SF₆ injection will be performed during all tests, (CARB will supply all personnel for analysis and monitoring of SF₆ test, contractor will provide an injection port into fuel line), e) contracting company must provide: the use of a CU with all necessary personnel for its operation, all process information (rates, temperatures, flame temperatures, concentrations, etc.), and access to CARB for a stack test. Assume that CARB will gather samples during regular working hours only.

Estimated \$6,000/week

PART II. - QUESTIONNAIRE

NAME OF COMPANY -

NAME OF COMBUSTION UNIT - CU-E

1. RANGE OF FIRING RATES OF THE PILOT SCALE COMBUSTION UNIT (CU) FOR A NOMINAL NO. 2 FUEL OIL.

.8 - 2.5 Million Btu/Hr

2. CORRESPONDING APPROXIMATE EXHAUST GAS FLOWRATE.

150 - 550 SCFM. (depends on excess air, exhaust gas flowrate is about 165 SCFM per 10^6 Btu/Hr heat input at 0% exhaust O_2 for No2 fuel oil)

3. FOR LIQUID FUELS, WHAT IS THE RANGE OF FUEL VISCOSITIES THAT CAN BE FIRED?

30 - 100 SSU @ 100°F currently we can only deliver the light fuel oil because of the multiburner arrangement. A heavy fuel oil delivery system could be designed and built for the unit.

4. CAN A TRACER GAS SUCH AS SF6 BE CONTINUOUSLY INJECTED INTO THE LIQUID FUEL STREAM (APPROXIMATELY 0.2 ML SF6 PER LITER OF FUEL)? IF SF6 CANNOT BE INJECTED INTO THE LIQUID STREAM DIRECTLY, ARE THERE POSSIBILITIES OF INJECTION NEAR THE BURNER?

Injection either into the fuel oil line or near the burner(s) is possible. Air or steam atomized nozzles can be used and the SF6 can be injected into this gas stream. Alternatively dual fuel nozzles are frequently used and the SF6 can be injected into the gas nozzle when firing on liquid fuels.

5. ARE PORTS AVAILABLE FOR FLAME TEMPERATURE DETERMINATION USING OPTICAL PYROMETRY? SUCTION PYROMETRY? DO YOU ROUTINELY MEASURE THE FLAME TEMPERATURE IN THE CU? WHAT TECHNIQUE IS USED?

3" diameter ports are located throughout the furnace for optical or suction pyrometry. Both bare (type R (Pt-Pt/Rd) thermocouples and suction pyrometers are routinely utilized in the facility. When no cooling surface is installed in the

unit bare thermocouples yield results very close to suction pyrometry temperatures. Flame impingement is simulated by directing the burner (and flame) at the cold well or placing the cold wall in the path of the flame.

6. CAN FLAME IMPINGEMENT ON A COLD SURFACE BE SIMULATED? PLEASE DESCRIBE. CAN A COLD WALL QUENCH BE SIMULATED? IF SO, PLEASE DESCRIBE THE PLACEMENT OF THE QUENCHING WALL AND HOW THE COLD WALL IS COOLED.

Yes to both. Either water cooled or Dowtherm/(100-500 F) cooled panels have utilized in the CU. These panels may be fabricated with any surface area depending on the requirement of the experiment and placed at any position within the firebox. Generally a serpentine pattern for the cooling path is chosen. The coolant enters and exits through two (or more) of the numerous ports located within the CU.

7. CAN THE INJECTION OF THE COMBUSTION AIR BE STAGED FOR THIS CU? PLEASE DESCRIBE.

Yes. Again the numerous ports can be used to inject staging air into the CU. A multiport manifold allows the staged air to be controlled and measured to any location within the CU. This staged air is preheated to the temperature of the main combustion air.

8. WHAT IS THE RANGE OF SWIRL NUMBERS AVAILABLE ON THE CU BURNER FOR COMBUSTION OF A NOMINAL NO. 2 FUEL OIL?

Because this unit is tangentially fired there are either 4 or 8 fuel inlets. Some swirl is imparted to the air immediately surrounding the fuel nozzle. However, most of the combustion air is introduced in an axial manner but tangential to the main firebox. This tangent angle may be varied to change firebox aerodynamics.

9. COULD A FAILURE OF THE CU BURNER ATOMIZER BE SIMULATED? PLEASE DESCRIBE.

If an air or steam atomized nozzle is utilized the easiest way to simulate a failed nozzle is to reduce or turn off the atomizing air. With a pressure atomized nozzle an oversized nozzle could be used to produce large fuel droplets.

10. CAN THE TEMPERATURE HISTORY OF THE GASES IN THE POST FLAME REGION BE OBTAINED?

Yes, again access ports are available over the whole length of the combustor and into the convection passages. Thermocouples or a suction pyrometer can be used at any of these ports to obtain both radial and axial temperature profiles.

11. IS WALL TEMPERATURE DATA AVAILABLE?

Yes; there are 5 thermocouples embedded in the walls, 1" below the surface in the flame region.

12. IS IT POSSIBLE TO CHANGE THE VOLUME OF THE CU BY BOLTING ON ANOTHER SECTION? HOW LONG WOULD IT TAKE TO CHANGE THE CU VOLUME? BY WHAT PERCENTAGE CAN THE ORIGINAL VOLUME OF THE CU BE CHANGED BY THE BOLT-ON SECTION(S).

It is possible to change the combustion volume to some extent by inserting heat transfer surface down into the combustion volume. Alternatively sampling could be made within the combustion volume at locations which represent various residence times. By the former technique the volume could be reduced by about 20%. By the latter technique the effective volume could be varied by a factor of two.

13. HOW MANY PORTS ARE AVAILABLE FOR SAMPLING ALONG THE POST FLAME REGION?

There are 18 ports throughout the combustion volume. The ports vary in size from 1" to 3".

14. PLEASE DESCRIBE DATA GATHERING/ANALYSIS CAPABILITIES THAT ARE AVAILABLE FOR CU TESTS (REAL TIME TEMPERATURES/FLOW/GAS CONCENTRATION INFORMATION, COMPUTER PLOTS, STATISTICAL INFORMATION, ETC.).

All temperatures (thermocouple read-out) are continuously monitored by an Apple Computer-based data acquisition system. All mass flows are determined by orifice/manometer sets and the data manually fed to the computer for determination of mass flow and storage of the data. There is continuous sampling of O_2 , CO_2 , CO , NO_x , SO_2 and TUHC. These values are recorded continuously on strip chart recorders and an additional set of data is manually fed to the computer for storage, manipulations and later retrieval. Particulate sampling (Method 5), modified Method 5 trains for semivolatile organics and VOST trains for volatile organics are also available. The data stored in the Apple Computer to be manipulated for analysis or plotting via a link to an X-Y plotter.

15. IS THERE A COMPUTER MODEL FOR THIS CU AVAILABLE? WHAT PARAMETERS CAN BE MODELED?

Equilibrium and kinetics combustion codes are available to predict gaseous specie concentrations as a function of time.

16. ARE BURNERS THAT SIMULTANEOUSLY INJECT BOTH LIQUID WASTE AND GASEOUS FUELS AVAILABLE FOR THE CU?

Dual fuel nozzles are routinely employed in the T-fired system.

17. IS A GAS BURNER AVAILABLE FOR THE CU?

Yes

18. THE FOLLOWING RELATE TO COMBUSTION OF SOLIDS IN THE CU. FOR THIS CU, ARE BURNERS AVAILABLE FOR COMBUSTION OF LIQUID SLURRIES CONTAINING SOLIDS, E.G., CAN THE EPA SOUP CONTAINING KITTY LITTER BE COMBUSTED? WHAT SOLIDS AND LIQUIDS HAVE BEEN TESTED? WHAT IS THE MAXIMUM PERMISSIBLE SIZE OF SOLIDS?

Solids containing slurries can be handled as long as the maximum particle size does not exceed the minimum orifice size in either the nozzle or fuel delivery system. Pressure atomized nozzles are limited to 100 μ m particle size. Air atomized nozzles can tolerate larger particles dependent on the nozzle design. The resulting viscosity of the slurry must also be evaluated to ensure pumpability. It may be necessary to pulverize any large solids. Alternatively special slurry handling systems could be designed to transport and atomize this material. If the slurries are to be introduced at the burner level the maximum particle size that can be injected into the facility without falling to the bottoms is limited to about 200 μ m. However, if the solids are injected above the burners such that they flow counter current to the main combustor flow, most any size can be handled. However, if the material contains large quantities of ash as large particles, provision may have to be made for continuous removal of this ash from the ash pit. An example of the above-burner solid injection was the cofiring of processed refuse derived fuel (RDF) with pulverized coal in this facility. In these tests the RDF was similar to shredded paper with a maximum size of 1-1/2" and was fed pneumatically to ports above the main coal nozzles. A special delivery system was designed for this fuel. Of course, pulverized coal is also routinely pneumatically fed to the CU. The coal grind in this case is a standard utility grind of 70% through 200 mesh.

Pulverized solid solvent refined coal with a similar grind to regular coal was also successfully fired in this CU. Special water cooled nozzles were incorporated to prevent coking at the nozzle however.

19. PLEASE ESTIMATE THE COST CHARGED TO CARB TO RUN A TEST FOR ONE WEEK (MONDAY TO FRIDAY). ASSUME: a) A PRACTICE RUN ON MONDAY AFTERNOON, 4 DAYS A TEST, b) ONE CONTRACTOR SUPPLIED LIQUID FUEL (SPECIFIED BY CARB) WILL BE USED DURING THE ENTIRE WEEK, c) THE FOLLOWING FAILURE CONDITIONS WILL BE SIMULATED (IF POSSIBLE): ATOMIZER FAILURE, WALL OR FLAME IMPINGEMENT QUENCH, HIGH EXCESS AIR, LOW EXCESS AIR, d) SF6 INJECTION WILL BE PERFORMED DURING ALL TESTS, (CARB WILL SUPPLY ALL PERSONNEL FOR ANALYSIS AND MONITORING OF SF6 TEST, CONTRACTOR WILL PROVIDE AN INJECTION PORT INTO FUEL LINE), e) CONTRACTING COMPANY MUST PROVIDE: THE USE OF A CU WITH ALL NECESSARY PERSONNEL FOR ITS OPERATION, ALL PROCESS INFORMATION (RATES, TEMPERATURES, FLAME TEMPERATURES, CONCENTRATIONS, ETC.), AND ACCESS TO CARB FOR A STACK TEST. ASSUME THAT CARB WILL GATHER SAMPLES DURING REGULAR WORKING HOURS ONLY.

One week (5 working days) of testing will cost \$10,500. This includes one full time test engineer, one full time and one half-time facility technician, one half-time facility supervising engineer, equipment use fees and fuel.

This cost does not include expenditures for facility set-up and preparation (e.g. installation of water wall panels placement of staged air manifolds, procuring test equipment and fuel, developing a test plan). These costs are very project specific, but are generally at least as much as that noted above for actual testing.

Post test costs (data reporting, returning the facility to an appropriate base configuration, etc.) are also not included in the above, and can be as much as a single week of testing.

PART II. - QUESTIONNAIRE

Name of Company

Name of Combustion Unit

CU-F

1. Range of firing rates of the pilot scale combustion unit (CU) for a nominal No. 2 fuel oil. 200,000-600,000 Btu/hr total; divided between the kiln charge ($< 200,000 \frac{\text{Btu}}{\text{hr}}$), kiln auxiliary flame (up to 250,000 Btu/hr), after burner flame (up to 90,000 Btu/hr) and backfired refractory heating channels (up to 60,000 Btu/hr).
2. Corresponding approximate exhaust gas flowrate.
50-160 SCFM (Wet basis)
3. For liquid fuels, what is the range of fuel viscosities that can be fired?
To 130 SSU (=28cS) for nozzle firing (fuel preheat capabilities are available). Any direct charging onto kiln floor.
4. Can a tracer gas such as SF₆ be continuously injected into the liquid fuel stream (approximately 0.2 ml SF₆ per liter of fuel)? If SF₆ cannot be injected into the liquid fuel stream directly, are there possibilities of injection near the burner?
Since SF₆ is a gas it cannot be put directly into the liquid fuel stream. SF₆ can however, be injected near the burner.
5. Are ports available for flame temperature determination using optical pyrometry? suction pyrometry? Do you routinely measure the flame temperature in the CU? What technique is used?
Yes. Flame temperatures are normally characterized by suction pyrometry. Solids burning temperatures are characterized by use of a fiber optic based two color pyrometer.

6. Can flame impingement on a cold surface be simulated? Please describe. Can a cold wall quench be simulated? If so, please describe the placement of the quenching wall and how the cold wall is cooled?

A water-cooled surface can be inserted into the flame zone.
A cold wall quench is not appropriate for this facility.

7. Can the injection of the combustion air be staged for this CU? Please describe.

Staging air can be injected at the entrance to the afterburner so that the entire kiln can be run under fuel rich conditions.

8. What is the range of swirl numbers available on the CU burner for combustion of a nominal No. 2 fuel oil?

0-2.5

9. Could a failure of the CU burner atomizer be simulated? Please describe.

Yes, Oversized or altered nozzles could be used to generate off-design spray patterns. Malvern Laser diffraction and spray rigs are available to quantify the changes to droplet size and spatial distribution.

10. Can the temperature history of the gases in the post flame region be obtained?

Yes, by suction pyrometry. The afterburner region is specially designed to provide sampling access.

17. Is a gas burner available for the CU?

Yes

18. The following relate to combustion of solids in the CU. For this CU, are burners available for combustion of liquid slurries containing solids, e.g., can the EPA soups containing kitty litter be combusted? What solids and liquids have been tested? What is the maximum permissible size of solids?

Solids may be charged onto the kiln floor in a batchwise fashion. Containerized waste can also be charged in specially designed fiber packs. Liquids & Sludges can be pumped into the kiln or loaded via the solids charging system.

19. Please estimate the cost charged to CARB to run a test for one week (Monday to Friday). Assume: a) a practice run on Monday afternoon, 4 days of tests, b) one contractor supplied liquid fuel (specified by CARB) will be used during the entire week, c) the following failure conditions will be simulated (if possible): atomizer failure, wall or flame impingement quench, high excess air, low excess air, d) SF6 injection will be performed during all tests, (CARB will supply all personnel for analysis and monitoring of SF6 test, contractor will provide an injection port into fuel line), e) contracting company must provide: the use of a CU with all necessary personnel for its operation, all process information (rates, temperatures, flame temperatures, concentrations, etc.), and access to CARB for a stack test. Assume that CARB will gather samples during regular working hours only.

Estimated: \$9,000/week

PART II. - QUESTIONNAIRE

Name of Company

Name of Combustion Unit

CU-G

1. Range of firing rates of the pilot scale combustion unit (CU) for a nominal No. 2 fuel oil.

45-80 KBtu/hr

2. Corresponding approximate exhaust gas flowrate.

12-22 scfm (wet basis)

3. For liquid fuels, what is the range of fuel viscosities that can be fired?

- No lower limit
- Upper limit: 130 SSU (=28 cS). Limited by atomization, however fuel may be heated to attain this viscosity.

4. Can a tracer gas such as SF₆ be continuously injected into the liquid fuel stream (approximately 0.2 ml SF₆ per liter of fuel)? If SF₆ cannot be injected into the liquid fuel stream directly, are there possibilities of injection near the burner?

Since SF₆ is a gas under these conditions, its introduction into the liquid fuel line would degrade nozzle performance. However, SF₆ can be doped into the air stream of the twin-fluid nozzle. The SF₆ will enter the CU at the same point as the fuel under this arrangement.

5. Are ports available for flame temperature determination using optical pyrometry? suction pyrometry? Do you routinely measure the flame temperature in the CU? What technique is used?

Yes. Eleven ports are available along the flame and post-flame zones for temperature measurements. Suction pyrometry is the normal technique used for CTT temperature measurements.

6. Can flame impingement on a cold surface be simulated? Please describe. Can a cold wall quench be simulated? If so, please describe the placement of the quenching wall and how the cold wall is cooled?

Flame impingement on a cold surface can be simulated by insertion of a water-cooled coil into the reactor. Insertion of cooled walls cannot be easily accomplished in this unit.

7. Can the injection of the combustion air be staged for this CU? Please describe.

A radial air injector can be placed at either of the two staging ports shown on the figure.

8. What is the range of swirl numbers available on the CU burner for combustion of a nominal No. 2 fuel oil?

0-2.4

9. Could a failure of the CU burner atomizer be simulated? Please describe.

Yes. Reduction in atomizing air flow would cause degradation of atomization quality. The larger dropsizes resulting from this procedure are representative of worn or failed atomizers. The degree of spray degradation can be characterized by our Malvern laser diffraction particle size analyzer.

10. Can the temperature history of the gases in the post flame region be obtained?

Yes, by suction pyrometry.

11. Is wall temperature data available.?

Yes. The wall temperature has been extensively characterized.

12. Is it possible to change the volume of the CU by bolting on another section? How long would it take to change the CU volume? By what percentage can the original volume of the CU be changed by the bolt-on section(s).

This is not practical for this CU.

13. How many ports are available for sampling along the post flame region?

Eleven

14. Please describe data gathering/analysis capabilities that are available for CU tests (real time temperatures/flow/gas concentration information, computer plots, statistical information, etc.).

Reactor flows:

- Atomizing air.
- Fuel (liquid or solid)
- Primary air flow
- Secondary and Tertiary air flows

Temperature:

- Thermocouples can be located throughout system.

Composition:

- CO₂
- CO
- O₂

15. Is there a computer model for this CU available? What parameters can be modeled?

A two dimensional heat transfer model is available which will allow prediction of gas and wall temperature profiles from input conditions. This state-of-the-art Monte Carlo model has recently been extended to allow prediction of waste destruction.

16. Are burners that simultaneously inject both liquid waste and gaseous fuels available for the CU?

Yes

17. Is a gas burner available for the CU?

Yes

18. The following relate to combustion of solids in the CU. For this CU, are burners available for combustion of liquid slurries containing solids, e.g., can the EPA soups containing kitty litter be combusted? What solids and liquids have been tested? What is the maximum permissible size of solids?

Slurried fuels have been burned in the CTT. Testing to date has involved mainly pulverized oil or coke emulsified in water or oil. Nozzles are available for up to 300 μ m particle size.

19. Please estimate the cost charged to CARB to run a test for one week (Monday to Friday). Assume: a) a practice run on Monday afternoon, 4 days of tests, b) one contractor supplied liquid fuel (specified by CARB) will be used during the entire week, c) the following failure conditions will be simulated (if possible): atomizer failure, wall or flame impingement quench, high excess air, low excess air, d) SF₆ injection will be performed during all tests, (CARB will supply all personnel for analysis and monitoring of SF₆ test, contractor will provide an injection port into fuel line), e) contracting company must provide: the use of a CU with all necessary personnel for its operation, all process information (rates, temperatures, flame temperatures, concentrations, etc.), and access to CARB for a stack test. Assume that CARB will gather samples during regular working hours only.

Estimated \$6,000/week

PROJECT 2

AN ANALYSIS OF THE USE OF SURROGATE COMPOUNDS IN HAZARDOUS
WASTE INCINERATION

by

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Acknowledgements

The author is deeply indebted to the many scientists and engineers that have taken part at one time or another in reviewing or providing guidance to the California Air Resources Board's hazardous waste incineration test program. Hopefully, their ideas have been integrated into this analysis accurately. The names of the individuals are presented below in alphabetical order.

Dr. Roger Atkinson, UC Riverside
Mr. Richard Brown, Acurex Corporation
Dr. Larry Caretto, CSU Northridge
Dr. Richard Flagan, California Institute of Technology
Dr. David Golden, Stanford Research Institute
Dr. Simon Goren, UC Berkeley
Dr. John Holmes, California Air Resource Board
Dr. John Kramlich, EER, Inc.
Dr. Chung King Law, UC Davis
Dr. Howard Mason, Acurex Corporation
Mr. Robert Mournighan, Environmental Protection Agency
Dr. David Ollis, North Carolina State University
(formerly at UC Davis)
Dr. Otto Raabe, UC Davis
Dr. Gary Samuelsen, UC Irvine
Dr. Randy Seeker, EER, Inc.
Dr. Wing Tsang, NBS
Dr. Larry Waterland, Acurex Corporation
Dr. Dean Wolbach, Acurex Corporation

The assistance of Mr. Richard Corsi and Mr. Nelson Sorbo in carefully reading this manuscript is appreciated.

Special thanks are due to Mr. Dean Simeroth, Mr. Robert Adrian, Mr. Peter Ouchida and Mr. Joe Pantalone of the CARB for their continued guidance and support of this project. This study was funded by CARB contract #A4-159-32

List of Acronyms and Selected Technical Terms

AIT - Autoignition temperature

CARB - California Air Resources Board

CBC - Circulating bed combustor

DE - Destruction efficiency

DRE - Destruction and removal efficiency

EFFM - Experimental flame failure mode

Exothermic - A reaction which releases heat

GPTS - Gas phase thermal stability

Hc/g - Heat of combustion per gram molecular weight

IDT - Ignition delay time

NBS - National Bureau of Standards

PAH - Polynuclear aromatic hydrocarbons

PCDD(s) - Polychlorinated dibenzodioxin(s)

PCDF(s) - Polychlorinated dibenzofuran(s)

Penetration - fraction of a compound fed to an incinerator which exits the incinerator. It is numerically equivalent to (1-DE)

PIC(s) - Product(s) of Incomplete Combustion

POHC(s) - Principal Organic Hazardous Constituents(s)

Refractory - resistant to treatment; especially capable of enduring high temperature.

SSD - Stationary Source Division

TFMK - Theoretical flame mode kinetics

THC - Total (unburned) hydrocarbons

TSHiO₂ - Gas phase thermal stability in an oxygen rich environment

TSLoO₂ - Gas phase thermal stability in an oxygen deficient environment

ABSTRACT

The California Air Resources Board has been studying appropriate methods for permitting hazardous waste incinerators. This study discusses various methodologies for selecting surrogate compounds for trial burns and the results of a series of three tests to evaluate pilot and full-scale incinerators firing wastes containing "surrogate" principal organic hazardous constituents (POHCs). The combustion units examined were a circulating bed combustor, a cement kiln and a sulfuric acid regeneration furnace. These units were operated in such a way as to produce optimum as well as poor combustion conditions. Although the combustion units were purposely selected to differ from one another, a number of surrogate compounds used to "spike" the wastes were common to all tests (CCl_4 , $\text{C}_6\text{Cl}_3\text{H}_3$). This procedure allowed limited comparison of the units and identification of the induced failure conditions which resulted in poor POHC destruction efficiency (DE) and formation of products of incomplete combustion (PICs). These data, in light of recent combustion research on modes of thermal destruction failure, have provided some bases for selecting appropriate surrogate compounds for use in evaluation of liquid injection waste incinerators. A selection of surrogates based upon a range of volatility, anticipated PICs and difficulty of destruction as measured by several incinerability ranking indices is recommended.

An Analysis of the Use of Surrogate Compounds in Hazardous Waste Incineration

Introduction

The California Air Resources Board (CARB) is currently developing guidelines for permitting hazardous waste incinerators. The purpose of this analysis is to present one approach to the problem which utilizes "surrogate" compounds to evaluate the efficiency of the combustion unit in destroying the principal organic hazardous constituents (POHCs) of a waste. An attempt will be made to explain the rationale behind such a methodology in laymen's terms. The report will be broken down into five sections as follows:

- I. Motivation for using surrogates
- II. Incinerability ranking scales
- III. Application of incinerability concepts to the selection of surrogate POHCs
- IV. Surrogates for continuous monitoring of incinerator performance
- V. Recommendations

I. Motivation for Using Surrogates

One definition of the term "surrogate" is "something that acts as a substitute". This is the broad sense of the term as used in this report. Why is it necessary to seek substitutes for hazardous constituents in a waste? Can't the POHCs simply be measured directly? The answer to that question is no in some cases and not without large expenditures of resources in a majority of others. Typically a single series of tests on an incinerator, with relatively detailed laboratory analyses

ranges from about fifty up to several hundred thousand dollars and involves months of planning and several weeks of field tests. Several problems exist: a) the waste streams are complex mixtures that rarely have consistent composition; b) incineration of the waste involves the possibility of many complex chemical reactions, so that even if one could identify and measure the POHCs in the waste and effluent gases, additional hazardous products of incomplete combustion (PICs) might appear; c) specific monitoring instrumentation, similar to a carbon monoxide (CO) analyzer, does not exist for the vast majority of POHCs or PICs. Given the magnitude of the problem and the lack of currently available technical solutions, we are forced to seek alternatives as a practical matter.

The central concept for surrogate use is that difficult to destroy surrogate POHCs could be carefully selected to challenge the incinerator's destruction efficiency (DE). These surrogates could be "spiked" into the waste at sufficiently high concentrations to assure their detection in subsequent analyses performed on samples of the flue gas effluent. By such means it would be possible to determine to what degree they had been destroyed. Furthermore, with appropriate selection of the POHCs, chemical analytical difficulties would be diminished (Tsang and Shaub, 1983) and an indication of PIC formation could also be obtained. Use of these surrogate POHCs would help to reduce analytical costs and provide better quantification of DE and PIC formation by reducing variability of waste stream composition. However, surrogate POHCs do not solve the problem of continuous monitoring of incinerator performance as it is not possible currently to measure the vast majority

of potential surrogate POHCs on a continuous basis.

There are a number of questions regarding the utility of surrogate compounds such as, "How does one select them?", "What assurance is there that if the surrogates are destroyed that all POHCs are destroyed?", "If the surrogate POHCs cannot be measured continuously, how does one know that the incinerator is continuing to function properly after the tests are performed?" In the ensuing sections, the use of incinerability ranking scales is discussed in the context of surrogate selection, and potential problems with the use of surrogate compounds are addressed.

II. Incinerability Ranking Indices

The purpose of an incinerability ranking index is to order compounds by a measure of the difficulty of their thermal decomposition. Based on such an ordering one could attempt to predict which constituents in a waste stream would be refractory. If it could be shown that the most refractory compound on an index achieved a certain level of destruction efficiency (DE), then presumably all other compounds would have an equal or higher DE. Thus it could be argued that it would only be necessary to determine the DE of the most difficult or a few of the most difficult to destroy compounds, reducing the analytical complexity of the test.

Numerous ranking scales have been proposed (Dellinger, 1985). Depending upon the ranking methodology employed, the specific order differs, in some cases very significantly. Clearly then, it would be necessary to demonstrate a correspondence between the ranking procedure and actual field test results from full-scale incinerators before the methodology could be applied with confidence. Following Dellinger (1985), a brief discussion of the basis of several of the ranking metho-

dologies is presented below:

- A. Heat of Combustion (Hc) - "The heat of combustion of a substance is defined as the enthalpy change for a reaction in which one mole is completely reacted with oxygen (Crumpler et al., 1981). The hypothesis behind this hierarchy is that those compounds with a large heat of combustion per gram molecular weight (Hc/g) will produce a higher flame temperature due to the exothermicity of combustion reaction. Presumably, the higher the flame temperature, the greater the destruction efficiency of a compound. Conversely, those compounds with low Hc/g will be poorly destroyed due to low flame temperature. A ranking of Hc/g for listed compounds is presented in the US-EPA Guidance Manual for Hazardous Waste Incineration Permits."

[Because this ranking method is the basis for the RCRA permitting methodology it has been widely applied, but highly criticized for using an equilibrium thermodynamic property, Hc/g, to rank incinerability when it is well known that incomplete thermal decomposition is often related to reaction kinetics.]

- B. Autoignition temperature (AIT) - "Autoignition temperature is the lowest temperature at which a combustible material in the presence of air begins to self-heat at sufficient rate to produce combustion without any other source of ignition (Cudahy and Troxler, 1983). Laboratory studies have shown a correlation between gas phase thermal stability and autoignition temperature (Lee et al., 1983). As a result AIT has been

suggested as a possible ranking scheme. The lower the AIT, the easier the substance is to decompose. The basis for its applicability would appear to be related to the self heating properties of the waste and its [ability] to sustain radical chain reactions."

[Autoignition temperature as measured by the standard test method cannot take into account mixing processes that occur in real combustion devices. Furthermore, the waste is typically a dilute constituent of the primary fuel which will govern the ignition properties of the mixture. Ignition, as measured in the test, usually takes place at temperatures which do not reflect the reaction rates that would be expected in real flames.]

- C. Theoretical flame mode kinetics (TFMK) - "Theoretical flame mode kinetics (TFMK) focuses on estimation and extrapolation of elementary reaction rate data that is available from experiment and theory (Tsang and Shaub, 1982). Only a small number of compounds may be ranked using this approach due to limited data. The approach is based on calculations that predict thermodynamically complete oxidation of most POHCs below 500°C. In contrast, field and laboratory results show incomplete oxidation at temperatures greater than 700°C for most substances. This implies that kinetics and not thermodynamics is controlling the rate of destruction of the compounds."

[In principle, the TFMK methodology could be applied more

widely if the sequence of events leading to incomplete destruction efficiency in an incinerator could be postulated or was known, e.g., incomplete vaporization of fuel droplets with subsequent low local O_2 environment. The major obstacle to application of the method is that the kinetic data base would have to be expanded, to cover the larger range of compounds found in hazardous wastes. The need for a larger data base is not unique to this method and would be required for the other experimental ranking methodologies as well. Additionally, a more general application of the TFMK method would require a level of chemical sophistication upon the part of the user in order to properly postulate the dominant reaction pathway, e.g., unimolecular (decomposition) bimolecular (radical attack) reaction, complex fragmentation, etc. and whether oxidizing or reducing conditions were applicable.]

- D. Experimental flame failure mode (EFFM) - "The experimental flame failure mode (EFFM) approach is generally based on experimental determination of destruction efficiencies in bench scale flame systems (Kramlich et al., 1983). However, under this approach as originally proposed, the compound ranking may vary depending on the "failure mode" or upset conditions of the flame. Four failure modes have been identified: poor mixing of waste and air, poor atomization of the waste, low flame temperature, and quenching of reactant waste by contact with cool surfaces or makeup air. Only five compounds were originally ranked, but recent laboratory studies have generated additional

data and rankings based on flame speed in a flat flame burner (VanDell and Shadoff, 1984)."

[This approach recognizes the importance not only of reaction kinetics, but of non-homogeneities in the flame zone as well. It is capable of capturing incomplete mixing and poor atomization quality, but does not take into account post-flame reactions. Because each of the failure modes may generate a different order, it is clear that several experiments would have to be performed for each compound studied. It should be noted that the two studies cited by Dellinger as falling into the EFFM category, Kramlich et al. and VanDell and Shadoff, are very different in nature. The latter used pre-mixed surrogate/oxidizer combinations and passed them through a hydrogen flame. The system was used to study effects of stoichiometry (relative amounts of fuel and oxidizer) on flame speed only, and not mixing processes or temperature inhomogeneities.]

- E. Ignition delay time (IDT) - "The ignition delay time of a hazardous organic compound or mixture is defined as the interval between an initial exposure to a step change in temperature and the principal exothermicity of the reaction as indicated by a rapid increase in temperature and pressure of the mixture (Miller et al., 1983). These times may be measured in shock tube experiments. The basis of the approach is that ignition delay is controlled by, and inversely proportional to, the reaction kinetic rate. Thus the smaller the IDT of a substance, the greater ease with which it [can] be

incinerated."

- F. Gas Phase Thermal Stability (GPTS) - "A ranking has been previously proposed based on laboratory determined thermal stability specified by the temperature required for 99% or 99.99% destruction at 2.0 seconds reactor residence time in an atmosphere of flowing air [$T_{99}(2)$ and $T_{99.99}(2)$], (Lee et al., 1982 and Dellinger et al., 1984). The basis for this approach is that any undestroyed material escaping the flame, must eventually be dealt with by thermal oxidation in the post-flame zone. It is proposed that the destruction of POHCs in the fraction of waste feed experiencing the flame environment is essentially the same for all organic compounds, i.e., greater than 99.999%. Thus, the differences in their measured DRE must be due to differences in their rate of destruction for the fraction of the waste escaping the rigors of the flame. This scale was originally developed for pure compounds in flowing air. However, recently generated data has shown that the relative stability varies as a function of the composition of the waste feed and oxygen concentration (Graham et al., 1985). This has led to modification of the rankings to account for the thermal stability of individual POHCs fed as a mixture in both an oxygen rich ($TSHiO_2$) and an oxygen deficient ($TSLoo_2$) environment. These hierarchies have been applied to predicting the results of studies described in the following paragraphs...."

[The GPTS methodology was applied to ten sets of full-scale

incinerator test data. A rank-order correlation test was applied to the data sets and it was determined that the order produced by the TSL O_2 ranking was statistically significant in seven of ten cases. Thus, the methodology shows promise. The fact that the TSL O_2 ranking was successful at all suggests that locally low O_2 conditions, caused either by incomplete mixing or slow volatilization from particulate matter that carries through the post-combustion zone, is a relatively common type of condition leading to reduced DE.]

One can see that each ranking method makes assumptions regarding the principal cause for low DE. Of particular note are laboratory experiments that have demonstrated that the order of incinerability following the flame zone changes with the mode of flame failure, consequently, it was deemed unlikely that any single ranking methodology would be universally applicable (Kramlich et al., 1983). Nevertheless, since most incinerators have high temperature post-flame zones with substantial residence time (> 1-2 seconds), the GPTS methodology applied to full scale incinerators was fairly successful in predicting the order of incinerability (Dellinger et al., 1985). Taken together, these studies suggest that it may be possible to select a group of surrogate POHCs from among the various ranking methodologies and which encompass the variety of "failure modes" leading to reduced DE. These compounds could be "spiked" into the actual waste in known quantities and analyzed in the effluent gases. Utilizing such a technique, it may not be necessary to find the most difficult to destroy POHCs, but simply one of the highly refractory POHCs for each type of failure condition.

Possible groupings of such compounds have been proposed for use in the EPA's incineration research program (Mournighan, 1984, 1985).

Thus far the discussion regarding surrogates has concentrated on the DE of POHCs. There is evidence to indicate that even if POHC DE is high, penetration of PICs can occur [Chang et al., 1985; Wolbach, 1985]. To understand this phenomenon, it is necessary to provide a brief layman's description of the nature of chemical reactions leading to the transformation of waste into thermodynamically stable products at room temperature, such as HCl, H₂O, and CO₂.

The decomposition of POHCs requires that chemical bonds be broken. Attack of a bond depends upon a POHC molecule's surrounding environment. At sufficiently high temperature a collision with an energetic molecule may transfer enough energy to the POHC to cause a bond to rupture (unimolecular decomposition). Alternatively, in flame environments there are very highly reactive chemical species (such as hydroxyl radicals HO·) which can attack specific bonds causing atoms to be pulled off the POHC (abstraction) or added onto the POHC (addition). Typically, a POHC molecule must go through many individual reaction steps before it is converted to simple molecules such as CO₂, H₂O and HCl. Each of these steps requires a certain amount of time and a suitable environment in order to occur. However, as soon as the first bond has been broken, the chemical identity of the POHC changes and it is considered to have been destroyed. If for some reason the remaining steps in the sequence cannot be completed, for example a sudden decrease in temperature (thermal quenching) or decrease in the concentration of radicals (H· atom scavenging by Cl· atoms), intermediate compounds such as CO,

chloromethane, benzene etc. can be formed from the corresponding parent molecule and can persist in the effluent. (A similar explanation accounts for the occurrence of CO and unburned hydrocarbons as PICs in the combustion of gasoline in an automobile engine.) In certain cases, e.g., in an environment with a local deficit of oxygen molecules, collisions of molecular fragments may result in the formation of compounds such as polynuclear aromatic hydrocarbons (PAH), soot and possibly dibenzofurans and dioxins. These PICs can also persist in the effluent stream if conditions are not present for their further destruction.

The environment in which POHC molecules find themselves differs dramatically from the flame zone to the post-flame zone. In the flame zone, very high heat release rates lead to very high temperatures which in turn lead to very high rates of chemical reaction, heat release and an abundant source of reactive "radicals" (atoms with unpaired electrons). The flame is maintained by a balance of the diffusion of fuel, waste and oxidizer to the flame zone in typical liquid injection incinerators. The radical population increase in the flame occurs because of "branching" reactions in which a greater number of reactive species are formed than are consumed in a reaction. Thus small concentrations of "radical scavengers", such as the Cl[•] atom from organochlorine compounds, can exert a large effect in the combustion process because they can tie up radicals and prevent them from participating in branching reactions. The rate of the reactions is also dependent upon the presence of sufficient oxygen to complete the chemical energy release and the formation of simple product molecules. The actual time spent in the flame environment is relatively small (typically less than

0.1 seconds), but because radical attack and unimolecular decomposition prevail at high temperature, very high DE is possible (> 99.999%) if conditions are optimal.

If for some reason, a POHC molecule escapes the flame reactions or PICS are formed by the flame, opportunities still exist to destroy the compounds in the post-flame zone. The post-flame zone is characterized by lower temperatures and very much lower radical concentrations so that unimolecular decomposition or complex fragmentation reactions predominate. Adequate time must be provided in order that reactions can be completed. As shown by Dellinger et al. (1985) the presence of oxygen also affects the decomposition rate of certain compounds so that some specific chemical bond attack probably occurs as well. Typical residence time, temperature and oxygen concentration in this region of an incinerator are of the order of > 1-2 seconds, > 800°C, and > 2% O₂, respectively. It should be pointed out that incinerators and high efficiency boilers differ in that boilers typically have relatively cold walls and reduced post-flame residence time in comparison to incinerators. Therefore, flame mode failures may be of much greater consequence in a boiler than in an incinerator.

Theoretically and based upon experiments in homogeneous systems, one does not expect to find appreciable amounts of POHCs or PICS in the flue gases of full-scale incinerators given typical average residence time, temperature, turbulence levels (mixing) and oxygen concentration. However, measurable concentrations of POHCs and PICS have been found in past studies and in the recently completed series of tests performed by the CARB. Neither the relative nor the absolute amounts remaining would

have been predicted by any single incinerability ranking scheme that has been proposed to date. These findings suggest that inhomogeneities are present in actual full-scale incinerator operation. The sources of inhomogeneities may be a) incomplete mixing of fuel and air caused by inadequate turbulent mixing or poor atomization quality, b) fluctuations in waste stream composition caused by immiscibility and phase separation, c) poor temperature or oxidant distribution which can again result from either waste inhomogeneity or lack of adequate turbulent mixing.

We are again led to the conclusion that single ranking methodologies are inadequate to predict either incinerator performance or the apparent relative difficulty of incinerability in full-scale combustion units. Individual differences in incinerator geometry, hardware, fuels, waste composition, etc., preclude a priori prediction of incinerator DE. Furthermore, DE of a surrogate does not provide information of itself regarding PIC formation. Bearing these shortcomings in mind, the succeeding section discusses an appropriate use of incinerability rankings.

III. Application of Surrogate POHCs

Surrogate POHCs need to be selected in such a way as to test the likely failure modes of each incineration system (Kramlich et al., 1984). The choice of the surrogate POHCs can be based upon incinerability ranking scales which are appropriate to the suspected failure modes. For example, suppose an atomization failure and subsequent poor O_2 distribution were suspected as likely candidate failure modes for a given incinerator. Then a difficult to destroy compound on both the EFFM (poor atomization failure) and the GPTS incinerability scales

(TSL₀O₂) should be selected as a surrogate POHC. In some cases, more than one surrogate POHC would need to be chosen in order to assure that the same physical conditions are experienced by the surrogate POHC(s) as the actual POHC(s) in the waste. The specific incinerator should then be tested with the actual waste spiked with low concentrations of the surrogate compounds. The concentrations of the surrogates should be kept as low as practical for the desired analytical accuracy in order not to disturb the spray combustion process.

It would also be desirable that some of the surrogate POHCs lead to partial decomposition products that are relatively easily identified PICs. For example it is likely that trichlorobenzene would yield chlorobenzene or benzene as a PIC or that Freon 113 (CF₃CCl₃) might yield Freon 12 (CF₂Cl₂) or Freon 11 (CFCl₃) as PICs. Thus, the presence of identifiable PICs in the waste would provide an assessment of the adequacy of conditions in the post-flame zone to assure complete combustion of any PICs that might have been formed by the flame chemistry.

To the extent possible, the surrogate POHCs should be selected with a view toward comparison with data obtained from other incinerator tests. The EPA has been developing a list of possible surrogate POHCs for use in its in-house and sponsored research programs (Mournighan, 1984, 1985). The surrogate approach can be validated if a sufficient database can be accumulated from the combined testing experience of many agencies on a variety of incinerator types. It is unlikely that a single surrogate "soup" will be applicable for all purposes, however, one or two surrogates in the mixture can still provide a benchmark for comparison of DE obtained.

Surrogate POHC "soups" can be best utilized for trial burns and compliance testing. They can reduce the analytical complexity associated with a test. Because they can be more precisely quantified, changes in incinerator performance should be more readily apparent in subsequent tests. Furthermore, since refractory POHCs would be selected for the "soups", one can have greater confidence that other compounds which might inadvertently appear in the waste stream will be destroyed. However, it is important to realize that surrogate POHCs are not a substitute for continuous monitors of incinerator performance. The problem of continuous monitoring of incinerator performance is discussed in the next session.

The rationale for the use of surrogates in CARB's recently completed tests of pilot and full-scale incinerators is summarized in Appendix A. It is provided to permit staff insight regarding the view of "combustion experts" on the evaluation problem. With the knowledge gained from those tests and more recent data on incinerability rankings, a few minor changes would probably be made in future tests, but the underlying concepts would remain the same.

IV. Continuous Monitoring of Incinerator Performance

There is virtually no disagreement among combustion experts regarding the ability of properly operated and maintained incinerators to destroy hazardous waste materials to acceptably low levels (>99.99 to >99.999% DE).¹ The difficulty is ascertaining that the incinerator continues to function properly at all times. Recognizing that this is an important problem, particularly regarding public acceptance of incineration, some suggestions have come forth regarding methods for

monitoring incinerator performance in the absence of specific continuous analyzers for POHCs.

The possible use of CO and THC as surrogate measures of incinerator performance has been proposed by several groups (Kramlich et al., 1983; Waterland, 1983; Chang et al., 1985; Kramlich et al., 1985; LaFond et al., 1985), and has been criticized by at least one other (Daniels et al., 1985). Waterland obtained pilot-scale data which indicated correlations of the fractional penetration of POHCs ($1-\%DE/100$) with CO and THC (see Figure 1). The EERC group (Kramlich et al. and LaFond et al.) have found that increases in CO preceded increases in the penetration of POHCs in a laboratory-scale turbulent flame reactor as parameters such as air/fuel ratio, atomization and degree of thermal quenching were varied (see Figure 2). At the same time, total unburned hydrocarbons (THC) tended to increase as POHC penetration increased. The recent CARB test of a pilot-scale circulating-bed combustor (CBC) (Chang et al., 1985) indicated that penetration of PICs appeared to be correlated with THC (see Figure 3) and that there were no instances of high PIC penetration without a corresponding increase in CO. The converse was not true, i.e., increases in CO were observed on some occasions without a corresponding increase in PIC penetration. POHC DE was high throughout this series of tests and did not appear to correlate well with either

¹ It is understood that acceptability of an incinerator's performance should not be limited to high DE, but should depend upon total emissions and their impacts upon the exposed population and environment.

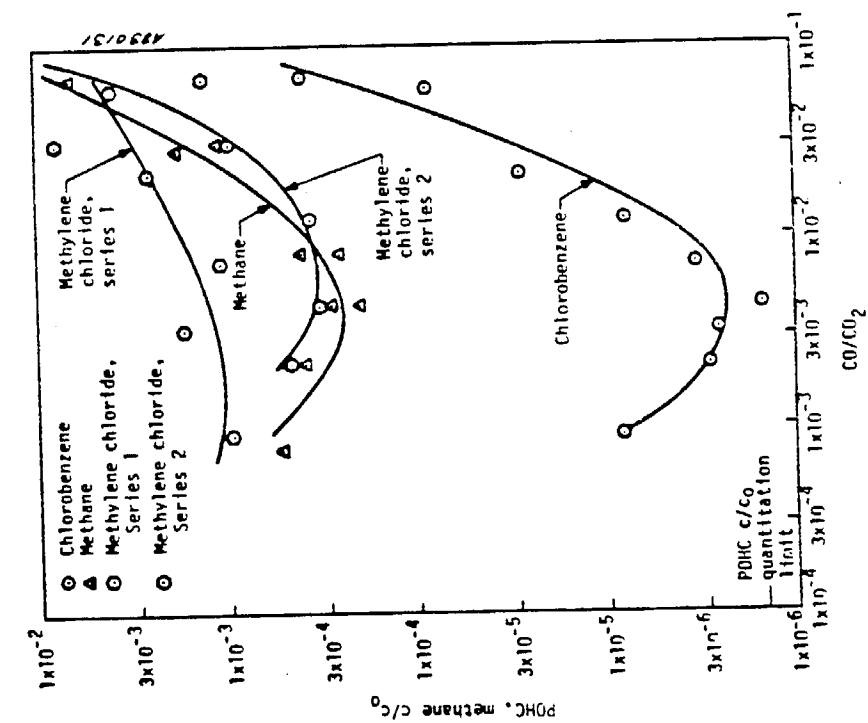


Figure 1a POHC and methane c/c_0 versus CO/CO_2 .

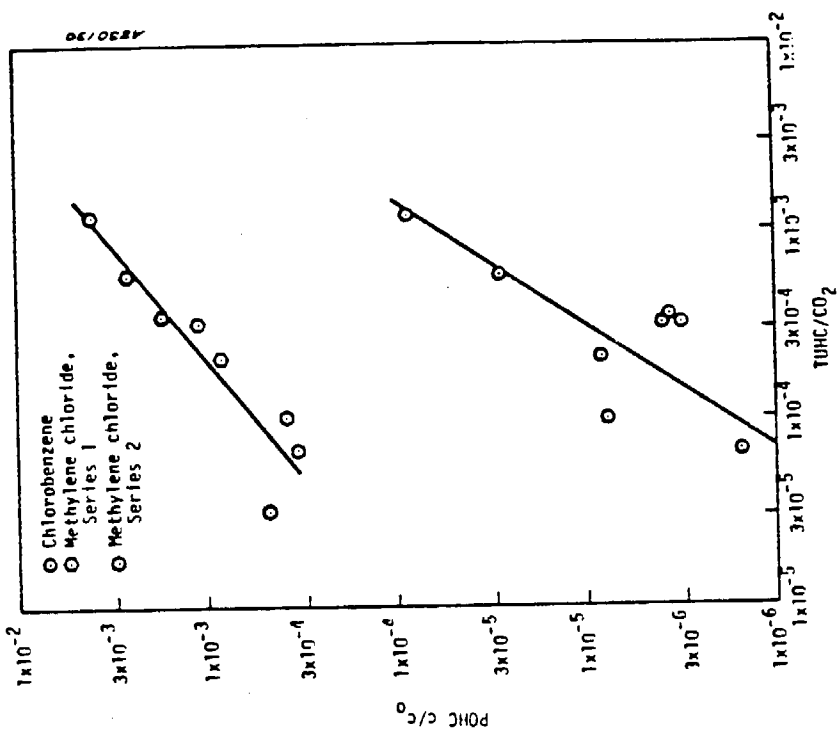


Figure 1b POHC c/c_0 versus $TUHC/CO_2$.

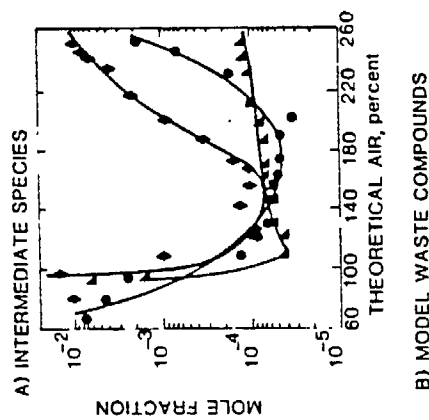


Figure 2a Influence of stoichiometry (3.8 lph fuel flow): \bullet total hydrocarbons, \blacktriangle CH_4 , \blacklozenge CO, \square acrylonitrile, \circ chloroform, \triangle benzene, \diamond chlorobenzene.

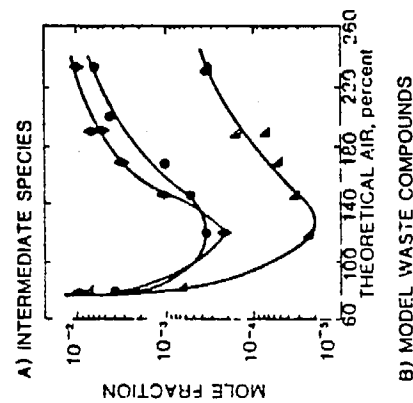


Figure 2b Effect of flame quench (3.8 lph fuel flow): \bullet total hydrocarbons, \blacktriangle CH_4 , \blacklozenge CO, \square acrylonitrile, \circ chloroform, \triangle benzene, \diamond chlorobenzene.

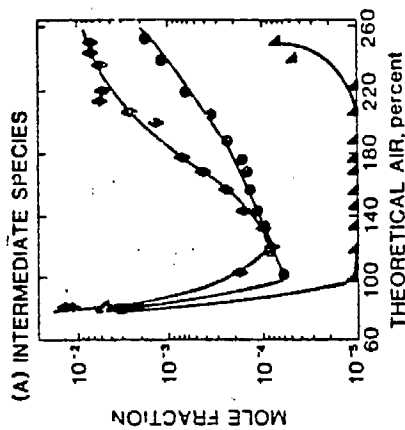


Figure 2c Impact of atomization quality (3.8 lph fuel flow): \bullet total hydrocarbons, \blacktriangle CH_4 , \blacklozenge CO, \square acrylonitrile, \circ chloroform, \triangle benzene, \diamond chlorobenzene.

Adapted from LaFond et al. (1985).

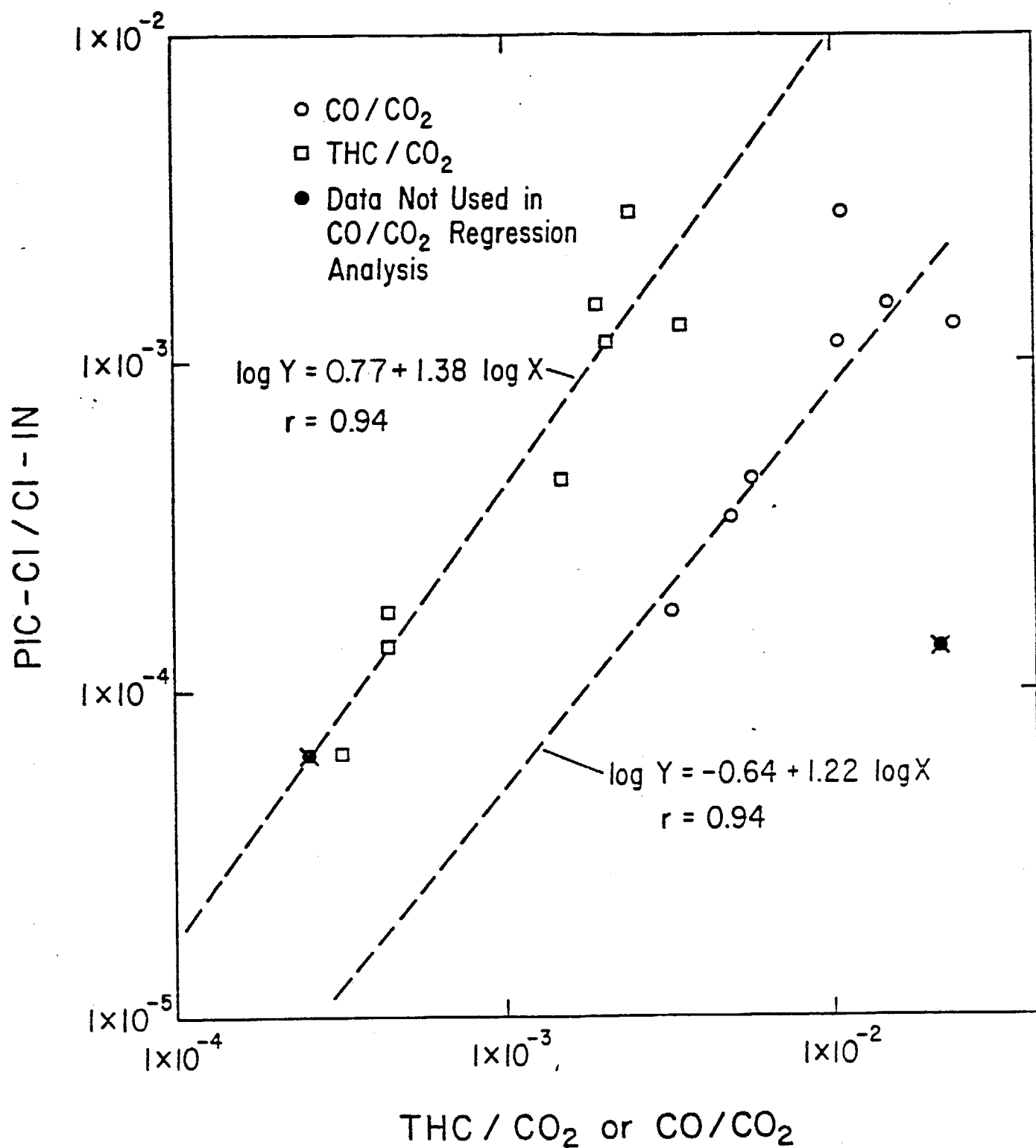


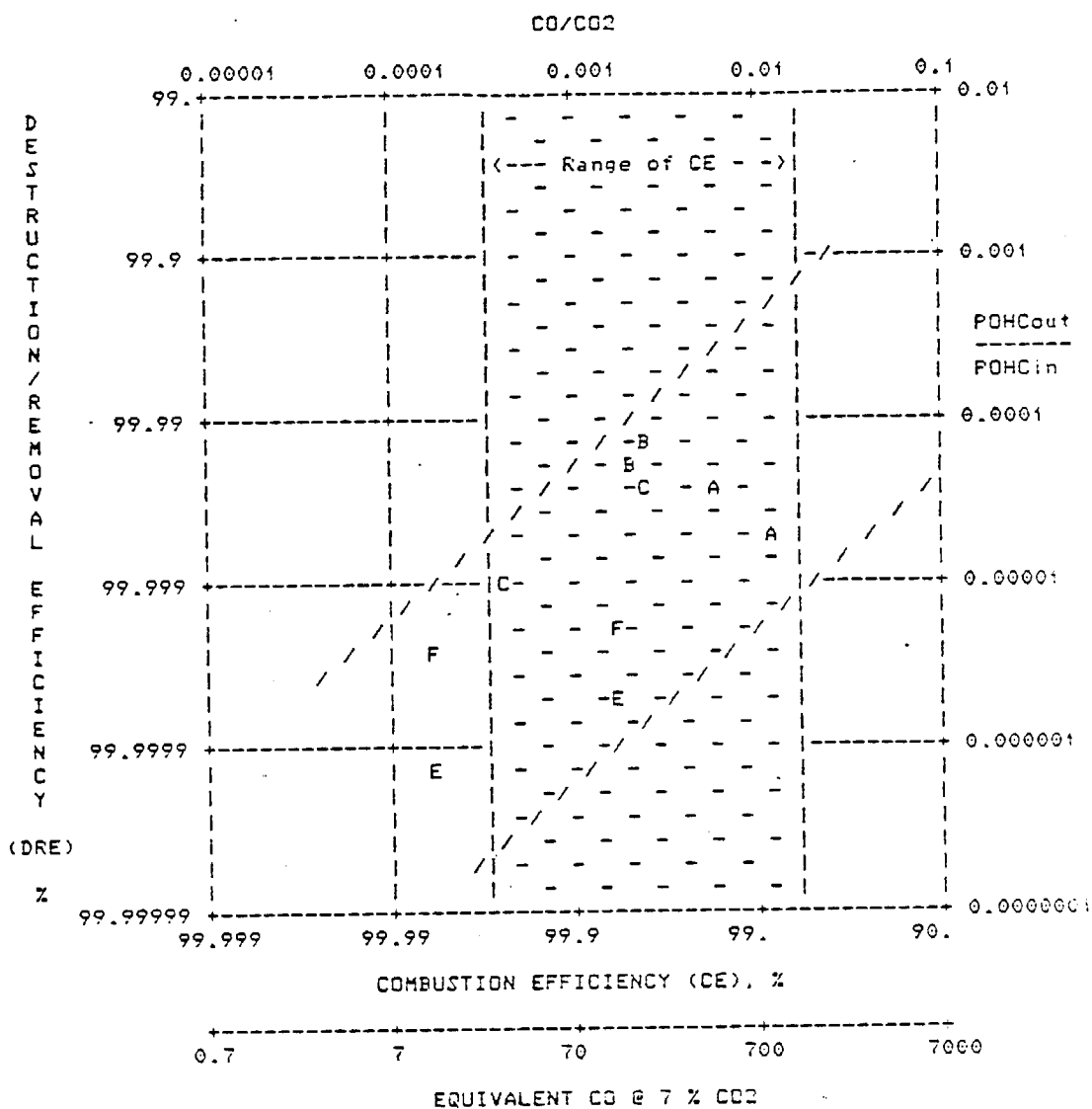
Figure 3 Correlation of Volatile PIC Chlorine Normalized by Total Fuel Chlorine Input Versus THC or CO Concentration Normalized by CO_2 Concentration.

Adapted from Chang et al. (1985).

THC or CO. Daniels et al., (Dow Chemical Company) although critical of the use of CO as a surrogate for POHC DE or as an indicator of incinerator performance, presented data obtained from a full-scale rotary kiln, which in 5 out of 6 cases indicated increased POHC penetration with increased CO concentration (see Figure 4). Considering that there were only two data points for each POHC tested, the trend appears to be real. Daniels et al., also acknowledged that CO might be useful as a lower bound upon POHC DE, but claimed that POHC DE and CO concentration were not related.

To understand these studies, one must keep in mind that CO is a normally occurring intermediate of hydrocarbon combustion processes, i.e., either the fuel molecules or the POHC can serve as a source of CO. Formation of CO is consistent with either high or low DE of POHCs, i.e., fuel and/or POHC molecules could have been destroyed even though some CO remains, because of the way in which POHC DE is defined. Nevertheless, persistence of moderately high values of CO (> 200 ppm) is normally indicative of incomplete combustion. It is believed that CO is one of the most stable intermediates formed in the combustion process and that its rapid oxidation is dependent upon a reasonable supply of hydroxyl radicals (HO^\bullet) (Wark and Warner, 1981). Thus its persistence in the post-combustion gases is either indicative of conditions where fuel or POHCs have escaped the flame zone (e.g., incomplete vaporization of fuel droplets), unfavorable conditions in the flame itself (e.g., low concentrations of flame radicals due to radical scavenging or insufficient temperature), low oxygen availability (poor mixing), or rapid temperature quenching which "freezes" its concentration (as occurs in

Figure 4 Combustion vs. Destruction/Removal Efficiency
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The POHC's selected for this series of trial burns were:

- A - 1,1,1-Trichloroethane
- B - Trichlorobenzene
- C - Carbon tetrachloride
- D - Silicon tetrachloride
- E - 2,4 - Dichlorophenol
- F - 2,4,6-Trichlorophenol

*Rotary-kiln incinerator burning a variety of feeds.

Adapted from Daniels et al. (1985).

internal combustion engines). CO tends to be a conservative measure of DE and can justifiably serve as a surrogate in the sense of a bound, but not as a one-to-one correlation with POHC DE.

There should be a greater likelihood that CO would correlate with PIC penetration when CO concentrations are high, indicating a partial oxidation of waste and fuel has occurred. However, because most PICs are more readily destroyed than CO, a correlation between CO and PIC penetration may not occur. Furthermore, CO is a thermodynamically stable specie at elevated temperature and its equilibrium concentration can be "frozen in" by rapid temperature quenching. This could also be a reason for lack of correlation with PIC formation. Thus, while an upper limit on CO can serve as a conservative bound of POHC DE, the limiting value should probably be determined for each combustion device based upon tests conducted with the POHC "soups". This is the current practice recommended by the EPA (Vogel et al., 1983).

In addition to the use of CO as a monitor of incinerator performance, we believe that continuous THC and O₂ monitors are necessary as well. THC tends to be a measure of the total amount of un-oxidized material remaining in the combustion gases. Therefore THC tends to rise as soon as there is incomplete combustion. The source may be the fuel, the waste or both. Increases in THC could give the incinerator operator an indication of impending problems in the system before a CO alarm is sounded. Similarly, diagnostic information might be provided to the incinerator operator by O₂ measurements and can suggest the steps that need to be taken to improve the combustion conditions, e.g., high CO and THC can result from too much air (quenching by excess air) as

well as from insufficient air! A recent report to the EPA has concluded that these continuous monitors can be successfully adapted to hazardous waste incinerators with proper sample conditioning (Podlenski et al., 1984).

Beside the use of CO, THC and O₂ analyzers as continuous monitors of incinerator performance, Tsang and Shaub (1983) have suggested continuous addition of surrogate compounds into the waste stream and development of sensitive, specific, continuous analyzers to quantify DE. At this time such systems do not exist although at least one such instrument is in developmental stages (continuous analyzer for sulfur hexafluoride, SF₆, Tracer Technologies, Escondido, CA). An approach would be to continuously add into the waste stream an extremely refractory compound, e.g. SF₆, which essentially escapes the incinerator unscathed. At the same time a second refractory, but more readily destroyed compound would be added in known proportion to the first. From measurements of both and their known ratios entering the unit, a continuous measure of incinerator performance would be obtained and obviate the need for precise blending of the surrogate with the waste. While the concept is appealing, there are a few practical problems to be worked out. One of which is that in a recent test, SF₆ appeared to have been quantitatively destroyed while some PICs still appeared in the combustion gases (California Air Resources Board, 1985). A possible explanation for this result was that the unit was firing solid fuels (coke). Thus carbon burn-out from fuel particles may not have been complete even though conditions were appropriate for the complete destruction of the SF₆. The fuel particles might have provided a locally reducing environ-

ment throughout the length of the incinerator, and recombination reactions with chlorine atoms, which is a documented phenomenon (VanDell and Shadoff, 1984), could have been the source of the observed PICs. This again emphasizes the need for selection of surrogate compound which pass through the same potential failure modes as the actual POHCs of concern. The alternative of periodic sampling, by integrated bag samples or by use of traps for volatile or semi-volatile compounds, does not appear to be a viable one for compliance monitoring purposes. Such sampling could not provide feedback in sufficient time to take corrective actions. It could fail to capture the events that lead to increased POHC penetration and PIC formation, and its expense would be unwarranted for the information returned. In a research situation, such a sampling method might be desirable because samples could be drawn specifically when continuous analyzers indicate a potential problem. Results could then be correlated to determine the ranges of the continuously monitored parameters which lead to increased penetration of POHCs or PICs.

V. Summary and Recommendations

In this report we have attempted to explain the rationale and a method for applying surrogate POHCs for acceptance and compliance testing of hazardous waste incinerators. The reasons for using surrogate compounds can be summarized as follows:

- A. It is difficult and in some cases impossible to quantify the concentration of a POHC in a waste or in combustion gases, and because of variations in waste composition, accurate measurement of POHC DE may not be possible. Use of surrogates impro-

ves analytical precision and accuracy, and permits quantitative measurement of surrogate DE. It also reduces resource requirements.

- B. No single index of incinerability adequately ranks the most difficult to destroy compound in full-scale incinerator tests. Since most incinerators have high temperature post-flame zones, the GPTS methodology based upon the TSL_{O_2} scale has met with some success. However, the EFFM results indicate that a wider range of surrogates to test additional incinerator failure conditions should be utilized.
- C. Surrogate POHCs that are more difficult to destroy than POHCs in the waste stream can be identified using a variety of incinerability ranking methodologies. By careful selection of surrogates to "spike" into the actual waste, a variety of potential failure conditions can be tested. Such a procedure provides a degree of conservatism in the event that a refractory POHC, not in the original waste stream during an acceptance test, inadvertently finds its way into the wastes. It is recommended that this procedure be continued.
- D. Formation of PICs is not directly measured by POHC DE. Careful selection of surrogates can provide readily measurable PICs in the event conditions are present favoring their formation.
- E. At this time, use of surrogate POHCs cannot assure that an incinerator is functioning properly on a continuous basis.

- F. CO is a refractory intermediate formed in the combustion of both fuel and wastes. As such, its presence in combustion gases is not a sufficient condition to presume low POHC DE. Nevertheless there are good reasons to suspect that occurrence of elevated CO concentrations are indicative of incomplete combustion and the presence of PICs. CO as a surrogate appears to be useful in setting an upper bound condition on POHC penetration, because its increase appears to precede that of POHCs in laboratory and some full-scale studies.
- G. Elevated THC can be attributed to both incomplete combustion of fuel or waste, so that like CO, it is not a sufficient condition to presume low DE. It appears to increase as POHC DE decreases in laboratory studies. Taken together with CO and O₂ analyzer readings it can serve as a diagnostic measure for the incinerator operator.
- H. Continuous monitors for CO, THC and O₂ are currently available, and with sample conditioning, can provide information regarding improper incinerator performance. Used in conjunction with surrogates during acceptance testing, a sufficient database might be developed, that greater meaning can be given to these analyzer readings. Acceptable absolute concentrations of these analyzer readings may vary from one incinerator to another, so that individual testing of each incinerator is needed to determine appropriate permit conditions. Requiring installation of these continuous monitors is recommended.

During the course of this analysis, several areas needing additional study have become evident. These are outlined below.

- A. Almost all the studies reviewed as part of this analysis dealt with liquid waste injection systems. Hence the conclusions of this report are strictly applicable only to such systems. There is very little information regarding the applicability of surrogates in slurries or solid fuels. It is imperative that research be initiated in these areas.
- B. Many of the incinerability ranking methodologies require an expanded data base. Although the GPTS methodology has a fairly extensive list of compounds, the number of compounds studied by the EFFM methodology is quite small. Extension of compounds studied by EFFM and validation on larger scale systems would be appropriate research studies.
- C. The NBS (principally Tsang and Shaub) has been engaged in the development of the TFMK methodology. It has not been widely applied because of the lack of kinetic and thermodynamic data. Although the NBS has moved to extend the list, a formal request from the State of California for such data might spur the effort. It is recommended that formal contact be made as it is believed that the NBS can be responsive to such requests for fundamental data and to supply guidance in its use.
- D. The lack of specific or even non-specific analyzers for haloge-

nated organics makes continuous monitoring of POHC DE untenable. Development of such analyzers continues to be a research need.

- E. Acceptance or compliance tests of full-scale incinerators typically yield data only under optimum combustion conditions. Under the CARB's current test program, the incinerators have been tested both under optimum conditions and under those which are considered to be beyond the limits of normal operation. Continued tests of this type are warranted in order to build the database for interpretation of continuous analyzer data.

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Appendix A

"Rationale for Selection of Surrogates Used in CARB Tests"

Introduction

This appendix provides the rationale behind the selection of surrogate POHCs used in three tests of possible hazardous waste incinerators. The tests were conducted by the CARB during the period from May, 1984 through March, 1985. A general discussion of all of the surrogate waste and fuel components utilized by the CARB is presented. This is followed by a brief description of each incinerator and the specific compounds used in its testing. A summary description of the findings that pertain to surrogate selection from each of the tests is then presented.

Surrogates Employed

The compounds which were utilized during the series of incineration tests are listed in Table A-1. They have been placed in approximate order of difficulty of destruction based upon the TFMK methodology of Tsang and Shaub (1982, 1983) for a homogeneous oxidizing flame environment. In addition, where data were available values of their heat of combustion, H_C , Appendix VIII rank, $TSHiO_2$ and AIT are given. Certain of the compounds in Table A-1 were components of the fuel which was used to provide heating value to the "spiking" soup. These have been marked with a single asterisk. Others were important PICs of the combustion process (benzene) and have been marked with a double asterisk. Tetrachloro-p-dibenzodioxin (TCDD) has been included for reference as a potential PIC of concern and has been marked with a "+".

General principles for the selection of the waste were laid out by the "expert" panels. These principles included the following list:

- a) Choose compounds which will be difficult to destroy based upon one or more ranking methodologies. Many of the compounds

Table A-1

List of Surrogate Compounds

Compound	TFMK Rank	-Hc (kcal/g)	App.VIII Rank	TSHiO ₂ (deg C)	AIT (deg C)	B.P. (deg C)
sulfur hexafluoride	1	-1.5	n.a.	n.a.	n.a.	-64
hexachlorobenzene	2	1.8	23	880	n.a.	309
benzene**	3	10.0	271	760	498	80
1,2,4 trichlorobenzene	4	3.4	64	790	571	213
TCDD #	5	3.4	65	n.a.	n.a.	n.a.
pentachlorophenol	6	2.1	28	n.a.	n.a.	309
toluene*	7	10.1	272	n.a.	482	111
xylene*	8	10.3	n.a.	n.a.	n.a.	138
ethylbenzene*	9	10.3	n.a.	n.a.	n.a.	136
carbon tetrachloride	10	0.8	2	820	n.a.	77
Freon 113	11	0.0	n.a.	n.a.	n.a.	48
1,1,1 trichloroethane	12	2.0	25	600	486	74

*Compounds of fuel added to provide heating value to the mixture.

**Important PICs of the combustion process.

#PIC of concern.

selected were organochlorines which have strong chemical bonds and which liberate the H atom scavenger, chlorine.

- b) Choose compounds which will pass through the range of combustion environments experienced by the actual waste. This amounted to selecting compounds with a range of volatility.
- c) Select at least one or two compounds which are in common with those from the EPA list of surrogate "soups" (Mournighan, 1984).
- d) Attempt to select those compounds which do not appear in substantial concentration in the actual waste to be fired or which can be expected to have high ambient background concentrations.
- e) Select compounds which can be readily analyzed and which could be expected to yield readily analyzable PICs.
- f) Consider availability and toxicity of the compounds and their likely PICs.

It can readily be seen that SF_6 , hexachlorobenzene, trichlorobenzene, carbon tetrachloride and Freon 113 would be highly ranked by one or more of the methods. In addition, they have a wide range of volatility and lead to detectable and difficult to destroy PICs such as benzene, toluene and chlorinated or fluorinated methanes. Pentachlorophenol was added in the third test to act as a specific precursor to the formation of the chemical classes of compounds dioxins and dibenzofurans. Given the quantity of waste needed, trichloroethane was substituted for Freon 113 in the third test based upon cost considerations and sample contamination problems encountered in the second test.

The compound of choice for supplying heating value to the surrogate "soup" was xylene which could be expected to yield the PICs toluene and benzene. As a practical matter, commercial grade xylene also contained ethylbenzene and lesser quantities of toluene. The presence of the toluene was unfortunate as it was expected to be a PIC. Its presence in

the original fuel as a POHC confounded data interpretation.

Discussion of Test Results

A circulating bed combustor (CBC) was selected by the SSD as the first unit to be tested. The unit was an experimental, pilot scale combustor owned and operated by GA Technologies, San Diego, CA. Since the unit was used for research and development purposes by GA, there was not an actual waste to be fed to the unit. Instead, a synthetic waste was selected by the expert panel in conjunction with GA and SSD staff. The components of that synthetic waste are presented in Table A-2. The waste was dynamically blended with water during the test, with the exception of one sample, to yield a heating value of about 8000 Btu/lb (19 MJ/kg).

POHC DREs and a variety of PICs were determined from chemical analyses of the bag (volatile compounds) and XAD-2 resin (semi-volatile compounds) samples. The most significant findings regarding surrogates are summarized below:

- a) The CBC was believed to have been operated in such a way that fuel-rich pockets of material periodically passed through the bed. This led to substantial levels of halogenated PICs such as chloromethane, chloroethene, Freon 11 and Freon 12 in the effluent gases. In addition substantial quantities of benzene and toluene were observed in the effluent. The occurrence of these particular PICs was not a surprise as they are themselves quite refractory compounds and logical intermediate compounds on the path to the stable oxidation products CO_2 , H_2O , HCl and HF .
- b) Total PIC formed in the combustor appeared to exceed 1×10^{-4} of the parent molecules input to the combustor, e.g., benzene and toluene emissions appeared to account for about 2-3% of the aromatic content of the synthetic waste. This served as a clear demonstration of the importance of controlling PIC formation and not solely DE of POHCs.
- c) The chlorinated volatile PICs chloromethane, dichloromethane and chloroethene appeared to correlate well with total unburned hydrocarbons (THC) and to a lesser extent carbon monoxide (CO) under the range of conditions that the CBC was tested.

TABLE A-2
INPUT FUEL ANALYSIS BY WEIGHT

Ethylbenzene	20.97%
Xylene	74.38%
Toluene	0.35%
Freon 113	1.00%
Trichlorobenzene	2.00%
Carbon tetrachloride	1.03%
Hexachlorobenzene	0.26%

Note: Sulfur hexafluoride added as gas.

- d) The penetration of fluorinated PICs, Freon 11 and Freon 12, appeared to be reasonably well correlated with the Freon 113 in the waste. All of the fluorinated compounds, including sulfur hexafluoride appeared to exhibit moderate dependence on temperature. A lesser correlation of Freon 113, Freon 11, and Freon 12 was observed with CO than with temperature. Based upon these observations, continued use of Freon 113 as a POHC would be desirable, as it yields characteristic PICs which can be determined readily by the CARB's El Monte laboratory.
- e) Sulfur hexafluoride was the most difficult to destroy POHC as would have been expected in this relatively low temperature combustion device (temperatures ranged from about 1350 to 1550 °F). However, its lack of correlation with any of the chlorinated organics, and its high correlation with CO makes SF₆ of lesser utility as a surrogate.
- f) Benzene is a likely intermediate in the decomposition of several of the POHCs in the synthetic waste, e.g., hexachlorobenzene, trichlorobenzene, ethylbenzene, xylene and toluene. Continued use of POHC precursors to benzene would be recommended as benzene has proven to be a recalcitrant compound to thermal destruction and is a pollutant of concern in its own right. However, improved sampling and analytical methods are needed for quantitative benzene determination.
- g) Carbon tetrachloride appeared to be readily destroyed. Its utility would be in yielding readily identifiable PICs such as chloromethane and dichloromethane. Otherwise, carbon tetrachloride did not appear to be an unusually difficult compound to destroy.
- h) The 1,2,4 trichlorobenzene appeared to be among the most refractory compounds in each of the three incinerator tests. Its analytic precision was the best of all of the semi-volatile POHCs in two of the three tests, indicative of reproducible recovery from the XAD-2 resin.

The second incinerator evaluated was a full-scale rotary kiln (560 feet long) used in the manufacture of cement. The kiln was normally fired with coke and natural gas or supplemental liquid organic waste amounting to as much as 25% of the total fuel heating value. For the purposes of the test, several different fuel compositions were evaluated: a) baseline-coke and natural gas, b) coke and 25% of heating value from the supplemental waste fuel, c) coke and 25% supplemental

waste containing the "spike" surrogate compounds, d) coke and 40% supplemental waste fuel containing surrogates, e) coke and a special low Btu waste mixture. The heating values and composition of the blended fuels are presented in Table A-3a and A-3b. As in the previous test, volatile compounds were determined by bag sample, and semi-volatile compounds by XAD-2 resin trap. Both types of samples were subjected to GC analysis. In addition, samples were drawn to determine dioxin and dibenzofuran concentrations by GC/MS.

Results from the test of the cement kiln were confounded by possible sample contamination. The normal waste stream contained several of the surrogate compounds even without their addition as a "spike" (e.g., carbon tetrachloride, Freon 113, and trichlorobenzene). This may have been a factor in the possible contamination of samples with Freon 113, trichlorobenzene and dichloromethane. Although the possibility of sample contamination appeared to be a problem in only a few samples, the number of samples drawn under a given test condition was small. Thus the conclusions that can be drawn from this test regarding the use of the surrogates must be viewed cautiously. They are listed below.

- a) Generally speaking, during the baseline tests, emissions of chlorinated organics appeared to be at about the same level as during the tests conducted with normal or spiked waste, i.e., within a factor of 2.
- b) Benzene and toluene emissions appeared to be slightly higher or the same during the baseline tests as during the normal waste or spiked waste tests. Given the high temperature environment and the long residence time in the kiln, thermal destruction of benzene was expected. A possible explanation for its occurrence in the exhaust gases is that it was volatilizing or formed in the locally reducing environment of individual coke particles which had not completed their "burnout" prior to exiting the kiln. Since more coke was being fired during the baseline tests, this would explain increased benzene and

TABLE A-3a Average Fuel Properties a/

	Coke ^{b/}	Normal Waste Fuel	Low BTU Waste Fuel	Natural Gas
BTU/lb (HHV)	15,383	12,300	7,660	23,748
Ash (%)	0.27	2.69	1.66	0
Sulfur (%)	0.96	0.11	0.07	0
Chlorine (%)	0.05	2.11	1.30	0
Carbon (%)	89.37	72.08	44.50	75
Hydrogen (%)	5.56	12.58	11.98	24
Nitrogen (%)	2.82	0.63	0.39	0
Oxygen (%)	0.97	9.86 ^{c/}	40.06 ^{c/}	0.75

a/ Information was supplied by Systech Laboratories.

b/ Dry Basis

c/ High oxygen content in fuel comes from water.

TABLE A-3b

Fuel Composition

(weight/percentages determined from a given volume)

Compound	25% Waste		Spiked Waste (25%) <u>1/</u>		Spiked Waste (40%) <u>1/</u>	Low BTU Blend
	Aug. 8	Aug. 13	Aug. 9	Aug. 10	Aug. 14	Aug. 13
Freon 113	0.55	1.95	15.8	11.5	3.19	0.44
Methylene-chloride ³	0.65	0.67	0.25	0.21	0.81	0.12
1,1,1-trichloroethane ³	2.50	1.44	0.83	1.13	0.40	0.79
Carbon tetrachloride	4	4	3.22	2.62	0.75	1.16
Benzene	N.D. ^{2/}	N.D. ^{2/}	N.D. ^{2/}	N.D. ^{2/}	N.D. ^{2/}	N.D. ^{2/}
Toluene	8.01	14.3	29.1	21.5	6.79	3.82
Ethyl benzene	3	3	3	3	3	3
Xylenes	5.94	23.0	28.5	28.8	16.6	9.56
Chlorobenzene ³	N.D.	N.D.	0.15	0.12	0.07	0.09
Trimethyl ₃ benzene ³	0.84	2.95	3.64	2.28	0.52	0.37
Trichloro-benzene	0.08	0.84	2.73	3.03	0.56	0.80

1/ Number in parenthesis is percent of total BTU needs supplied by waste fuel during test.

2/ N.D. = Not detected; detection limit is estimated at 0.01 weight to volume = percentage.

3/ Present in normal waste, not purposely blended.

toluene emissions compared to those periods when supplemental liquid waste was fired. If this hypothesis is true, then one can conclude that the surrogates selected for this test do not experience the same combustion history as solid particles. There would be a clear need for development of solid surrogates which can mimic such behavior.

- c) During one of the "failure mode" tests, i.e., low O_2 , slightly increased levels of benzene and toluene were observed in comparison with the 25% and 40% spiked waste tests. The highest benzene and toluene level observed in this test (bag sample) could possibly be associated with a corresponding "spike" in CO emission. A similar finding existed for one of the low Btu waste tests, but was not as distinct. Increased benzene and toluene emissions appeared to be associated with reducing conditions.
- d) There was no apparent correlation of non-criteria chlorinated organic emissions with average CO emissions or CO excursions, with the possible exception of trichlorobenzene. However, in the case of trichlorobenzene, possible sample contamination made all of the elevated TCB data suspect. It also appeared that CO was not consistently related to O_2 concentration, i.e., in some cases CO increased rapidly when O_2 increased rapidly and vice versa. It may be that CO in this system is formed by both insufficient air for combustion as well as by thermal quenching of the CO_2 dissociation reaction.
- e) Freon 113 and dichloromethane appear to have elevated values in comparison to other organics. In particular, both compounds appear to have elevated levels in the same samples. These data are highly suspect and are consistent with sample contamination. The source of the contamination was not isolated. Continued use of Freon 113 as a surrogate might be a problem as it may be present in many laboratory environments. Dichloromethane (methylene chloride) was not selected as a surrogate, but was present in the normal waste. Again, it is a common laboratory chemical, and its use as a surrogate is questionable for that reason.
- f) In contrast to the CBC test, SF_6 was quantitatively destroyed in the kiln. This was not surprising as the temperature regime was not limiting to the kinetics of the reaction. This observation again serves as a reminder that it is important that the surrogates selected as "spike" compounds pass through the same time/temperature/oxygen environment as the actual waste. In this case, the most refractory organics appear to have been destroyed efficiently (99.999%), those organics which appeared in the exhaust gases were probably either PICs or represent sample contamination problems.

The third incinerator evaluated was a full-scale sulfuric acid rege-

neration furnace. The unit differed from the earlier tests in that "spent" sulfuric acid, having little heating value, was the normal waste fired. Heat to sustain combustion was provided by firing natural gas in a "Dutch oven". Wastes were introduced from a rotary-cup atomizer at one end of the furnace at right angles to the burning gases exiting the Dutch oven.

Several waste mixtures were tested: a) "spent" acid alone, b) diesel fuel and perlite (an inert solid added to increase the viscosity of the mixture), c) "spent" acid spiked with a synthetic waste mixture containing the surrogate compounds (see Table A-4 for synthetic waste composition). The latter synthetic waste was to represent hazardous waste that the company desired to add to the spent acid to provide supplemental heating value to the mixture. The tests conducted can be broken down into three categories: a) "baseline" (spent acid only or with the diesel/perlite mixture), b) "normal" (spent acid and the spiked synthetic waste fed to the furnace under typical operating conditions), c) "low O_2 " (spent acid and spiked synthetic waste). Although the term "low O_2 " has been used to describe the last series of tests, it is something of a misnomer in that air and fuel feed rates were set by the operator based upon past experience and visual observation of the flame condition rather than by O_2 measurement. The "low O_2 " condition was the minimum acceptable to maintain the quality of sulfuric acid recovered by the process. Samples were drawn for analysis from two separate locations, the boiler exit and the stack. Samples drawn included bag samples for volatile organics, XAD-2 resin samples by MM-5 train for semi-volatile compounds, and a similar train for dioxins and diben-

TABLE A-4
SYNTHETIC WASTE COMPOSITION

Compound	Weight %
Tetrachloromethane	22.4
1,1,1 Trichloroethane	21.2
Pentachlorophenol	3.0
1,2,4 Trichlorobenzene	10.6
Diesel fuel	30.6
Methanol	1.2
Perlite	11.0

zofurans.

As with the cement kiln test, the quantity of data obtained was limited. Essentially no useful information regarding volatile compounds, primarily PICs, was obtained because too few samples were analyzed. Samples were drawn from two locations simultaneously, the boiler exit and the effluent stack. Duplicate samples were only drawn from the stack. Dioxin and dibenzofuran samples were also obtained at the boiler exit and at the stack. Because of the limited number of sampling trains available, no semi-volatile resin samples were drawn simultaneously with the dioxin and dibenzofuran trains, but the latter were obtained immediately following semi-volatile sampling. Results of those tests applicable to surrogate selection are discussed below.

- a) Freon 113 was detected in a few of the bag samples. Since it was not present in the waste stream, contamination of the samples was suspected. There is a small possibility that infiltration of ambient air downstream of the boiler could account for the presence of Freon 113, but it seemed less likely. Dichloroethane also exhibited anomalous behavior, i.e., higher concentrations observed in the stack samples than at the boiler exit. Again, contamination of the sample or infiltration of ambient air could possibly explain the observation.
- b) Benzene concentrations in the few available bag samples was near detection limits. This was in sharp contrast to the resin samples which indicated high benzene concentrations. In the previous two tests, reasonable agreement with bag and resin samples for benzene had been obtained, i.e., roughly within a factor of two for samples drawn over similar periods, which was about the same magnitude as the variability in benzene levels in duplicate resin samples. The probable explanation for this observation was attack of the resin by the highly acidic atmosphere. Continued measurement of benzene by both bag and resin samples is suggested, along with continued development of the resin method.
- c) DEs of the POHCs carbon tetrachloride, 1,1,1 trichloroethane and pentachlorophenol was high under all test conditions

(>99.999%). Because the DEs were so high, it was not possible to readily distinguish an order of difficulty of destruction, i.e., in situations of high DE, sample concentrations are typically near detection limits and meaningful ordering of data is not possible.

- d) The single outstanding observation of these tests was that 1,2,4 trichlorobenzene penetration increased as CO/CO₂ ratio increased. The agreement between the duplicate resin samples drawn at the stack was high for those samples above detection limits. In the samples at or below detection limits, both samples were consistently at or below detection limit. The simultaneously drawn individual boiler samples exhibited the same trend as the stack samples, and absolute concentrations were generally higher than the stack samples, as expected. The good success with trichlorobenzene in this and the CBC test suggest that it be retained as a surrogate POHC in all future tests. It has proven to be among the most refractory organochlorine compounds tested thus far.
- e) Pentachlorophenol was specifically added to this waste stream as a potential PCDD and PCDF precursor. There was no obvious relationship between the presence of pentachlorophenol and PCDD or PCDF formation, although small amounts of various PCDD and PCDF isomers were detected in some of the samples. Although it appeared that higher concentrations of PCDDs and PCDFs were formed when pentachlorophenol was present, total organochlorine content of the waste would have also increased. One anomalous stack sample containing PCDD and PCDF was obtained during which there was no pentachlorophenol and little organochlorine content in the waste. If this sample was incorrectly labelled either in the field or by the analytical laboratory, then it would appear that dioxin emissions increased as organochlorine content increased. (There was definite evidence that one set of samples was incorrectly labelled).
- f) It was not possible to relate the trichlorobenzene results to the PCDD and PCDF results as simultaneous sampling for both compounds did not occur. Furthermore, uncertainty regarding sample labelling remains as a confounding factor.

Summary

The utility of using refractory surrogate compounds was evident in the series of tests recently completed by the CARB. In several cases the composition of the waste stream was not known and would not have been constant. A synthetic waste mixture containing surrogate compounds

could be employed in such cases to provide a preliminary evaluation of the combustion unit. Even in those cases where an existing waste was available, it was not always possible to get a complete description of the waste. "Spiking" of known amounts of surrogate compounds into the waste allowed quantification of destruction efficiency and vastly reduced the complexities and costs of the chemical analyses. Even with the use of surrogates, chemical analytical difficulties were encountered.

Interpretation of the evidence obtained to date would suggest the continued use of 1,2,4 trichlorobenzene as a surrogate POHC. Besides being a refractory organic, its likely PICs, benzene and possibly toluene, are also highly refractory compounds. The occurrence of trichlorobenzene in the post-combustion gases was related to moderately low temperature combined with low oxygen levels, i.e., reducing environment. Benzene and toluene also appeared to be related to locally reducing environments.

Freon 113 appears to be subject to contamination problems. Nevertheless, it does yield readily identifiable, stable and refractory PICs such as Freon 11 and Freon 12. In wastes with little or no fluorine content, its continued use would be desirable in order to determine PIC formation. Efforts should be made to determine whether the analytical laboratory environment can be improved to reduce contamination.

Sulfur hexafluoride proved to be quite refractory under low temperature combustion conditions. However, it appeared to track temperature relatively closely and presumably would only be of utility under conditions where it was desirable to determine if there were

"cold" pockets for waste material to escape. Its physical properties do not lend themselves to introduction through liquid waste streams. As a continuous surrogate, it would have to be considered in the developmental stage and relatively expensive compared to temperature, CO, O₂ and THC monitors.

Pentachlorophenol would appear to be a good choice for a surrogate in cases where the PICs PCDD and PCDFs were to be evaluated. Further testing is needed, however, to establish whether it is the PCDD and PCDF precursor or whether other chlorinated arenes serve the same function (e.g. trichlorobenzene). A specific series of tests with one or the other compound in the waste would appear to be an appropriate goal of future research. Further research on PCDD and PCDF formation in general is needed. The tests conducted thus far have not been able to discern between PCDD and PCDF formation by precursor compounds or whether trace amounts can be formed simply as a result of the presence of sufficient chlorine in the waste.

Carbon tetrachloride and hexachlorobenzene POHCs have not appeared to be particularly difficult to destroy. The ease of destruction of carbon tetrachloride is understandable from TFMK predictions. The reason for hexachlorobenzene's apparent ease of destruction is not clear. Its dissolution and distribution into the waste mixture should be evaluated. The continued need to use these two compounds as surrogates is questionable at this point. This is particularly true because the range of volatility represented by these compounds can probably be achieved with less toxic substitutes.

The original incinerability rankings were developed for oxidizing

conditions. In all three of the tests in this series there was evidence that increased penetration was associated with low O_2 conditions. Future selection of surrogate mixtures should attempt to account for this. Furthermore, POHCs should be picked to yield readily identifiable PICs. The clear demonstration of high DE with simultaneous PIC formation in the CBC test should serve as a clear indication that the thermal destruction of a molecule is a sequence of reactions, not a single reaction. Good chemical understanding of the likely pathways of thermal decomposition can contribute to appropriate selection of surrogates.

Research involving suitable solid phase surrogates is needed. The cement kiln results suggested that gas and liquid phase refractory surrogate POHCs were destroyed with high efficiency. However, benzene and toluene appeared in substantial concentration in the effluent gases. Thus volatilization from the solid phase appears to be a potentially important route of escape from an incinerator. The CARB will likely be faced with evaluation of municipal solid wastes incinerators in the future and timely research should be initiated now.

Nitrogen containing compounds (acrylonitrile and acetonitrile) have been suggested as possible refractory surrogates. None of these were evaluated in the current series of tests. Analyses for aromatic PICs beside benzene and toluene were not performed. Given the likelihood that benzene and toluene will appear in normal wastes, an analysis for a chlorinated aromatic PIC such as chlorobenzene would be desirable. Additional laboratory tests with the above-mentioned compounds and an examination of the types of PICs formed is warranted.

PROJECT 3

NON-CRITERIA ORGANIC POLLUTANTS

by

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PREFACE

This project contains an analysis of the organic compound data obtained from a series of surrogate waste incineration tests which took place at the Stauffer Chemical Company, Dominguez Hills, in March of 1985. It represents an analysis prepared for the staff of the Stationary Source Division (SSD), Engineering Evaluation Branch, and was intended to serve as a basis for a section of a test report being prepared by the SSD. The analysis assumes that the reader has access to the additional test data and background information such as continuous analyzer readings, sampling times, sample train descriptions, etc. It has been included as a part of the Final Report for CARB Contract A4-159-32 for completeness, as it was one of the tasks performed under the contract at the request of the SSD.

This appendix was prepared by Dr. Daniel P.Y. Chang with the assistance of Mr. Richard Corsi. The author is indebted to the other members of the review panel which recommended and prioritized test conditions for the Stauffer Chemical Company's Dominguez Hills facility. These individuals were Dr. Simon Goren, UC Berkeley, Dr. G. Scott Samuelsen, UC Irvine, and Dr. Wing Tsang, National Bureau of Standards.

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NON-CRITERIA ORGANIC POLLUTANTS

The emission and fate of non-criteria organic pollutants are a major concern in the evaluation of waste incinerators. Although extensive sampling for organic pollutants took place, during the project many of the bag samples for volatile organics were not analyzed. In addition, results of some of the semi-volatile organic sample analyses were confounded by factors beyond the control of the sampling program as will be discussed in the following sections. The results of the laboratory analyses which were performed, and also deemed valid, are presented and discussed in this portion of the report as are their possible implications. Recommendations regarding future improvements in data capture are also presented.

Summary of Tests Conducted

Three different waste mixtures were fed to the sulfuric acid regeneration furnace. The first was the "spent acid" which was typical of the feedstock normally injected into the recovery furnace. Only a qualitative GC/MS survey of its composition was available. The results of that survey indicated the presence of chlorinated organics in parts-per-million concentration range. The second "waste" was actually a test mixture of diesel fuel and perlite which did not contain chlorinated compounds. The second "waste" was fed to the furnace at the same time as the "spent acid" to establish a datum for comparison with the third "waste". The third "waste" was a "spiked" synthetic mixture containing a fuel component, several chlorinated POHCs of interest and perlite. The composition of the mixture, hereafter referred to as "spiked synthetic waste", is presented in Table 1.

Table 1
Synthetic Waste Composition

Compound	Weight %
Tetrachloromethane	22.4
1,1,1 Trichloroethane	21.2
Pentachlorophenol	3.0
1,2,4 Trichlorobenzene	10.6
Diesel fuel	30.6
Methanol	1.2
Perlite	11.0

The tests conducted can be broken down into three categories: "baseline" (spent acid only or with the diesel/perlite mixture), "normal" (spent acid and the spiked synthetic waste fed to the furnace under typical operating conditions), and "low O₂" (spent acid and spiked synthetic waste). Although the term "low O₂" has been used to describe the last series of tests, it is a misnomer in that air and fuel feed rates were selected by visual observation of the flame condition by the operator, rather than by direct O₂ measurement. The "low O₂" flame condition was the minimum acceptable to the operator in order that the quality of sulfuric acid recovered by the process be maintained, based upon past experience.

Samples were drawn for analysis from two separate locations, the boiler exit and the stack. In this report, sampling location is denoted by a B (for boiler) or S (for stack) suffix following the sample number. Samples drawn included bag samples (BS) for volatile organics, XAD-2 resin samples by MM-5 train (RT) for semi-volatile compounds, a similar train for dioxins and dibenzofurans (DT), and an inorganic acid train (HT) for HCl emissions.

Results

The experimental results from the bag samples, resin samples, and the polychlorinated furan/dioxin analyses are presented below.

Bag Sample Results

The data collected on volatile organic compounds are shown in Tables 2a and 2b. Although over 100 bag samples were drawn during the course of the tests, only 17 of the bags analyzed corresponded to run

TABLE 2a
Volatile Organic Compound Summary

ARB No.	Dichloro- difluoro- methane	Dichloro- methane	Trichloro- fluoro- methane	1,1 dichloro- ethane	trans 1,2 dichloro- ethane	Trichloro- methane	Trichloro- trifluoro- ethane	1,2 dichloro- ethane
BS- 16 S 3-5-85 Normal	0.12	9.9	9.0E-02	<.10	<1.0	<.02	0.30	46.00
BS- 18 S	0.20	20.0	8.0E-02	<.10	<1.0	<.02	0.39	18.00
BS- 19 S	0.25	7.4	1.2E-01	<.10	<1.0	<.02	0.29	24.00
BS- 38 S 3-14-85 Low 02	0.33	17.0	4.9E-02	<.10	<1.0	<.02	7.80	<.10
BS- 40 S	0.38	27.0	8.0E-02	<.10	<1.0	<.02	2.40	0.23
BS- 24 B 3-5-85 Normal	<.02	15.0	5.3E-02	<.10	<1.0	<.02	8.60	4.40
BS- 26 B	0.10	17.0	1.2E-01	<.10	<1.0	<.02	5.70	10.00
*BS- 22 B 3-1-85 Blank	0.73	4.0	2.5E-01	<.10	<1.0	<.02	0.29	<.10
*BS- 23 B	<.02	7.3	2.1E-01	<.10	<1.0	<.02	1.40	0.48
*BS- 29 B 3-6-85	0.12	5.2	6.6E-02	<.10	<1.0	<.02	0.91	0.47
*BS- 30 B	0.019	<.6	<.01	<.10	<1.0	<.02	1.40	<.10
*BS- 67 B 3-14-85	0.037	<.6	<.01	<.10	<1.0	<.02	0.92	0.14
BLANK (2K5HSE1)	<.02	1.6	<.01	<.10	<1.0	<.02	0.03	<.10
BLANK (2K5HSE2)	<.02	10.0	<.01	<.10	<1.0	<.02	0.02	<.10
#1A ADMIN. PARKING	1.10	2.1	3.8E-01	<.10	<1.0	0.044	0.28	3.60
#2A EAST FENCE	1.10	1.4	2.5E-01	<.10	<1.0	0.036	0.61	0.96
#BAMB-17 SULFUR	0.87	6.7	1.6E-01	<.10	<1.0	0.033	1.20	1.10
#BAMB-18 FRT.GATE	0.36	5.4	1.9E-01	<.10	<1.0	0.038	1.50	0.34
#BAMB-20 OFFICE	0.50	7.0	1.5E-01	<.10	<1.0	0.035	1.50	0.81
#BAMB-19 SULFUR	0.74	5.5	1.7E-01	<.10	<1.0	0.046	0.43	0.68

TABLE 2a (Continued)

ARB No.	1,1,1 trichloro- ethane	Tetra- chloro- methane	Bromo- dichloro- methane	1,2 dichloro- propane	Trichloro ethane	Chloro- dibromo- methane	1,2 dibromo- ethane	Tribromo- ethane
BS- 16 S 3-5-85 Normal	1.10	2.5E-02	<.01	110.00	1.50	0.12	<.01	0.05
BS- 18 S	0.49	1.5E-02	<.01	30.0	0.52	0.08	<.01	0.36
BS- 19 S	1.50	4.3E-02	<.01	32.0	0.25	0.08	<.01	0.03
BS- 38 S 3-14-85 Low 02	0.75	2.6E-02	<.01	<0.1	0.14	<.01	<.01	<.01
BS- 40 S	1.60	4.3E-02	<.01	5.9	0.21	<.01	<.01	0.02
BS- 24 B 3-5-85 Normal	1.10	4.9E-02	<.01	13.0	0.19	0.07	<.01	0.02
BS- 26 B	2.10	6.2E-02	<.01	12.0	3.10	0.41	0.02	0.23
*BS- 22 B 3-1-85 Blank	1.70	2.8E-02	<.01	<.20	0.09	<.01	<.01	<.01
*BS- 23 B	2.30	3.8E-02	<.01	<.20	0.03	0.02	<.01	<.01
*BS- 29 B 3-6-85	0.33	1.3E-02	<.01	<.20	0.06	0.02	<.01	<.01
*BS- 30 B	0.13	<.01	<.01	<.20	0.04	<.01	<.01	<.01
*BS- 67 B 3-14-85	0.10	1.2E-02	<.01	<.20	0.02	<.01	<.01	0.01
BLANK (2K5HSE1)	0.12	<.01	<.01	<.20	0.33	<.01	<.01	<.01
BLANK (2K5HSE2)	0.23	<.01	<.01	<.20	0.10	<.01	<.01	<.01
*1A ADMIN. PARKING	0.79	9.2E-02	<.01	<.20	0.04	<.01	<.01	<.01
*2A EAST FENCE	0.95	2.5E-01	<.01	<.20	0.03	<.01	<.01	<.01
*BAMB-17 SULFUR	0.98	9.7E-02	<.01	0.6	0.05	<.01	<.01	<.01
*BAMB-18 FRT. GATE	1.40	9.0E-02	<.01	4.1	0.04	<.01	<.01	<.01
*BAMB-20 OFFICE	1.00	1.1E-01	<.01	3.1	0.17	<.01	<.01	<.01
*BAMB-19 SULFUR	2.70	9.1E-01	<.01	2.7	0.28	<.01	<.01	<.01

TABLE 2a (Continued)

ARB No.		Tetra-chloro-ethane	Benzene
BS- 16 S	3-5-85 Normal	12.00	<1.0
BS- 18 S		3.90	<1.0
BS- 19 S		4.20	<1.0
BS- 38 S	3-14-85 Low 02	2.50	<1.0
BS- 40 S		5.50	2.0
BS- 24 B	3-5-85 Normal	4.30	3.0
BS- 26 B		20.00	<1.0
*BS- 22 B	3-1-85 Blank	1.50	<1.0
*BS- 23 B		5.80	<1.0
*BS- 29 B	3-6-85	0.79	<1.0
*BS- 30 B		0.09	3.0
*BS- 67 B	3-14-85	0.06	<1.0
BLANK (2K5HSE1)		0.06	<1.0
BLANK (2K5HSE2)		0.05	<1.0
#1A ADMIN. PARKING		0.30	
#2A EAST FENCE		0.30	
#BAMB-17 SULFUR		0.33	<1.0
#BAMB-18 FRT. GATE		0.36	<1.0
#BAMB-20 OFFICE		0.79	2.0
#BAMB-19 SULFUR		1.30	4.0

REMARKS:

SAMPLE #1 LOC. B 2/26/85

SAMPLE #1A ADMIN. PARKING LOT LOG#18 1410 2/28/85

SAMPLE #2A EASTERN FENCE LINE LOG#19 1425 2/28/85

#BAMB-17 SULFUR PARKING LOT AMBIENT AIR DOWNWIND LOG #B144

#BAMB-18 FRONT GATE AMBIENT AIR UPWIND LOG #B145

#BAMB-20 AMBIENT AIR MAIN OFFICE UPWIND LOG #B147

*Fields blanks

All concentrations in PPB

TABLE 2b
Bag Sample Results
(STACK and BOILER)

ARB NO.	Date	Time	Test Condition	CARB TET Concentration (ppb) Penetration (fraction)	1,1,1TCA Concentration (ppb) Penetration (fraction)	Waste (#/min)	Flow (DSCFM)
BS-16S	3-5-85	1441-1447	Normal	0.03 8.7E-08 99.99999	1.10 3.5E-06 99.99965	7.0	1.389E+04
BS-18S	3-5-85	1611-1619	"	0.02 5.4E-08 99.99999	0.49 1.6E-06 99.99984	7.0	1.425E+04
BS-19S	3-5-85	1620-1626	"	0.04 1.5E-07 99.99998	1.50 4.9E-06 99.99951	7.0	1.425E+04
BS-38S	3-14-85	1029-1039	Low Oxygen	0.03 5.2E-08 99.99999	0.75 1.4E-06 99.99986	12.0	1.380E+04
BS-40S	3-14-85	1310-1322	"	0.04 8.9E-08 99.99999	1.60 3.0E-06 99.99970	12.5	1.482E+04
BS-22B	3-1-85	1530-1530	Baseline	0.03 n.a. n.a.	1.70 n.a. n.a.	-	1.284E+04
BS-23B	3-1-85	1334-1335	Baseline	0.04 n.a. n.a.	2.30 n.a. n.a.	-	1.284E+04
BS-24B	3-5-85	1344-1345	Normal	0.05 1.7E-07 99.99998	1.10 3.5E-06 99.99965	7.0	1.377E+04
BS-26B	3-5-85	1514-1515	"	0.06 2.2E-07 99.99998	2.10 6.7E-06 99.99933	7.0	1.389E+04
BS-29B	3-6-85	0845-0845	"	0.01 n.a. n.a.	0.33 n.a. n.a.	-	1.371E+04
BS-30B	3-5-85	0845-0845	"	<0.01 n.a. n.a.	0.13 n.a. n.a.	-	1.371E+04
BS-67B	3-14-85	1045-1045	Low Oxygen	0.01 6.1E-9 99.99999	0.10 6.5E-8 99.99999	12.0	1.380E+04

conditions. Of these, 5 appeared to be highly suspect because of their high detection limits and apparently poor sensitivity (the analytical column was changed after 2/28/85 and subsequent results were deemed of acceptable quality). The suspect bag samples have been discounted from this analysis and are not reported here. An additional 5 samples were field blanks. This left only 7 valid points, of which 5 were taken at the stack and 2 at the boiler exit. DEs and emission rates were calculated using the stack flowrate closest in time to when the sample was drawn. This assumption would not have materially changed DREs or emission rates as fuel and waste feed rates were held fairly constant throughout a given test day. DEs and corresponding penetrations for the two volatile POHCs, 1,1,1 trichloroethane and tetrachloromethane, are presented in Table 2b. The concentrations of all compounds which were routinely analyzed by the Haagen-Smit laboratories are presented in Table 2a. The results do not represent a complete analysis of all possible halogenated volatile organic PICs.

Resin Sample Result

The data obtained from the analysis of the resin trains appear in Tables 3a through 3c. The DEs and corresponding penetrations of the tetrachloromethane (CARB TET), 1,1,1 trichloroethane (TCA), 1,2,4 trichlorobenzene (TCB) and pentachlorophenol (PCP) have been computed when applicable. Flowrates at the boiler exit were assumed to be the same as those measured at the stack at the nearest corresponding test period.

The trichlorobenzene results appear to be of high quality. Duplicate samples exhibited little variability, quality control samples

TABLE 3a

Resin Train Sample Results
(STACK)

ARB NO.	Date	Time	Test Condition	CARB TET Concentration (ppb) Penetration (fraction) DE (%)	1,2,4 TCB Concentration (ppb) Penetration (fraction) DE (%)	1,1,1 TCA Concentration (ppb) Penetration (fraction) DE (%)	PCP Concentration (ppb) Penetration (fraction) DE (%)	Temperature Furnace (F) (K) (back)	Temperature Furnace (F) (K) (front)	Waste (#/min)	CO (ppm)	CO ₂ Dust Collector (%)	O ₂ (%)
RT-1S	2-27-85	1428-1528	Baseline	0.07	<0.06	0.63	0.06	1815 1264	1565 1125	-	25	10.3	1.5
RT-2S	2-27-85	1620-1720	"	0.16	<0.06	0.52	0.05	1821 1267	1567 1126	-	22	10.4	1.4
RT-3S	2-28-85	0948-1148	"	0.14	<0.03	0.20	<0.01	1815 1264	1229 938	-	25	11.4	2.2
RT-4S	2-28-85	0948-1148	"	0.05	<0.03	0.11	<0.01	1815 1264	1229 938	-	25	11.4	2.2
RT-5S	3-1-85	0910-1110	"	0.03	<0.03	0.14	0.02	1858 1287	1561 1122	-	25	11.4	2.2
RT-6S	3-1-85	0916-1116	"	0.02	<0.03	0.22	0.01	1857 1287	1558 1121	-	25	11.4	2.2
RT-7S	3-5-85	1423-1523	Normal	0.08 2.6E-07 99.99997	<0.06 <5.3E-07 >99.99995	0.42 1.3E-06 99.99987	0.03 1.5E-06 99.99985	1878 1299	1347 1004	7.0	25	10.2	1.8
RT-8S	3-5-85	1430-1530	"	0.11 3.9E-07 99.99996	<0.06 <5.0E-07 >99.99995	0.68 2.2E-06 99.99978	0.03 1.2E-06 99.99988	1878 1299	1347 1004	7.0	25	10.2	1.8
RT-9S	3-6-85	1048-1348	"	0.04 1.1E-07 99.99999	<0.03 <2.0E-07 >99.99998	0.13 3.3E-07 99.99997	0.03 9.7E-07 99.99990	1850 1283	1452 1062	8.9	32	11.4	1.9
RT-10S	3-6-85	1048-1248	"	0.06 1.7E-07 99.99998	<0.03 <2.0E-07 >99.99998	0.22 5.7E-07 99.99994	0.02 5.9E-07 99.99994	1856 1286	1473 1074	8.6	29	11.2	1.9
RT-11S	3-7-85	1218-1418	"	n.a. n.a. n.a.	<0.03 <1.6E-07 >99.99998	n.a. n.a. n.a.	n.a. n.a. n.a.	1833 1274	1597 1142	11.0	50	10.8	2.1
RT-12S	3-7-85	1215-1415	"	0.03 6.6E-08 99.99999	<0.03 <1.6E-07 >99.99998	0.06 1.1E-07 99.99999	<0.01 <1.9E-07 >99.99998	1833 1274	1597 1142	11.0	50	10.8	2.1

RT-14S 3-12-85	1118-1318	Low Oxygen	0.02 4.7E-08 >99.99999	0.71 4.0E-06 99.99960	0.19 3.9E-07 99.99996	<0.01 <2.1E-07 >99.99998	1428 1049	1867 1292	10.0	520	12.4	2.3
RT-15S 3-12-85	1116-1317	"	0.04 7.9E-08 99.99999	0.89 5.0E-06 99.99950	0.21 4.2E-07 99.99996	0.01 4.30E-07 99.99996	1428 1049	1867 1292	10.0	520	12.4	2.3
RT-16S 3-14-85	1002-1202	"	0.04 7.8E-08 99.99999	0.58 3.2E-06 99.99968	0.19 3.7E-07 99.99996	<0.01 <1.8E-07 99.99998	1604 1146	1710 1205	12.0	89	10.1	1.5
RT-17S 3-14-85	1000-1200	"	0.08 1.6E-07 99.99998	0.63 3.2E-06 99.99968	0.18 3.3E-07 99.99997	0.03 6.5E-07 99.99993	1604 1146	1710 1205	12.0	89	10.1	1.5

TABLE 3b

Resin Train Sample Results
(BOILER)

ARB NO.	Date	Time	Test Condition	CARB TET Concentration (ppb) Penetration (fraction) DE (%)	1,2,4 TCB Concentration (ppb) Penetration (fraction) DE (%)	1,1,1 TCA Concentration (ppb) Penetration (fraction) DE (%)	PCP Concentration (ppb) Penetration (fraction) DE (%)	Temperature Furnace (F) (K) (front)	Temperature Furnace (F) (K) (back)	Waste CO (#/min) (ppm)	CO2 Dust Collector (%)	O2 (%)	
RT-1B	2-27-85	1407-1607	Baseline	<0.01	<0.03	0.06	<0.01	1558 1121	1814 1263	-	29	10.4	1.3
RT-3B	3-1-85	0846-1056	"	<0.01	0.08	0.06	0.02	1561 1122	1858 1287	-	25	11.4	2.2
RT-4B	3-1-85	1313-1513	"	0.01	<0.03	0.01	<0.01	1545 1114	1859 1288	-	25	11.9	2.2
RT-5B	3-5-85	1321-1533	Normal	0.18 6.1E-07 99.99994	0.30 2.5E-06 99.99975	0.29 9.0E-07 99.99991	<0.01 <3.3E-07 >99.99997	1367 1015	1875 1297	7.2	25	10.4	1.8
RT-6B	3-6-85	1106-1322	"	0.28 7.5E-07 99.99992	0.26 1.7E-06 99.99983	0.04 9.9E-08 99.99999	<0.01 <2.7E-07 99.99997	1464 1069	1854 1285	9.0	30	11.3	1.9
RT-7B	3-7-85	1229-1429	"	0.11 2.3E-07 99.99998	0.09 4.7E-07 99.99995	0.21 4.2E-07 99.99996	0.01 2.9E-07 99.99997	1597 1142	1833 1274	11.0	50	10.8	2.1
RT-8B	3-12-85	1115-1334	Low Oxygen	0.04 9.2E-08 99.99999	0.44 2.5E-06 99.99975	0.07 1.5E-07 99.99998	0.02 5.9E-07 99.99994	1429 1049	1868 1293	9.8	475	12.4	2.3
RT-9B	3-14-85	0948-1201	"	0.67 1.4E-06 99.99986	1.88 9.4E-06 99.99906	0.84 1.6E-06 99.99984	<0.01 <2.1E-07 >99.99998	1604 1146	1710 1205	12.0	89	10.1	1.5

TABLE 3C

Field Blanks and Quality Control Analyses

ARB NO.	Date	Time	Mass collected in micrograms		CARB IET	1,2,4 ICB	1,1,1 ICA	PCP
			Test Condition	Test				
*RT-13S	3-8-85	1215-1415	Normal		0.21	<0.60	0.40	0.20
*RT-18S	3-13-85	0915-0935	Low Oxygen		0.39	0.60	7.10	0.20
QC-1	-	-	-		2.80	2.80	1.22	n.a.
QC-1	-	-	-		2.80	2.60	1.12	n.a.
QC-2	-	-	-		2.90	2.80	1.24	9.80
QC SOL	-	-	-		2.95	2.98	1.58	9.67
BLANK	-	-	-		0.06	0.12	0.25	n.a.

* = field blank

had good recoveries and field blanks were low. Trichlorobenzene concentrations measured at the stack under "low O₂" conditions were significantly higher than the TCB concentrations obtained under "normal" conditions (Student's "t" test applied to equality of the means of the two sets of samples at the 1% significance level).

There was greater sample variability (within a factor of about two between duplicate samples) for the tetrachloromethane in comparison to the TCB results. During common sampling periods, bag sample and resin train results are within an order-of-magnitude of one another in all cases. The interpretation of tetrachloromethane results was confounded because it also could have been formed in the combustion process from compounds such as trichloromethane [1]. Agreement between duplicate trichloroethane resin train samples was good, however, ambient air concentrations of trichloroethane and tetrachloromethane were detected in concentrations comparable to those in the stack in several samples, adding another confounding factor. Furthermore, one field blank (RT-18S) appeared to have been contaminated with trichloroethane. Thus it is possible that trichloroethane and tetrachloromethane samples drawn at the stack could have been elevated by ambient air infiltration. It should be noted that both the tetrachloromethane and the trichloroethane appear in comparable quantities in "baseline" tests utilizing only spent acid waste. However, boiler exit concentrations appear to be lower than stack emissions for samples drawn on the same days! This would suggest that either ambient air or quench water could have served as a source of these compounds, though the former would seem more likely. Pentachlorophenol concentrations were near detection limits in all cases and it is difficult to attribute any pattern to those data.

It should be noted that previous experience with collection of benzene on the XAD-2 resin suggested that it is possible to overload the resin [2]. Back-up resin traps were not used in this study. Furthermore there is a distinct possibility of resin degradation having occurred because of the high sulfuric acid concentration in the stack. Benzene was determined solely by elution time from the GC column and the possibility of other compounds co-eluting in the particular method used cannot be ruled out. This might explain a wide disagreement which was observed between the bag and resin data for benzene. Therefore, the benzene results obtained from the resin trains were not considered quantitative and have not been included in the summary.

Polychlorinated Furan/Dioxin Results

Four boiler-exit and four stack samples for polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) were drawn. Two field blanks were also prepared. The quantities of PCDFs and PCDDs were below or very near detection limits for all but three of the sample trains. The laboratory data sheets for those three trains are included in Exhibit A through D. The sum of detection limits and corresponding total PCDF and PCDD recovered from a given train are presented in Table 4. It should be noted that two samples with elevated concentrations were drawn from the boiler exit. Although small amounts of PCDDs and PCDFs were recovered from a few stack samples, they did not in general correspond to the same isomers recovered in the corresponding boiler samples. One elevated stack sample was drawn during a "baseline" test (DT-1S) when the suspect precursor compound pentachlorophenol was

California Analytical Laboratories, Inc.

POLYCHLORINATED DIOXIN/FURAN ANALYSIS

TICKET NO: 20421

EXHIBIT A

CLIENT ID: DT-2B- CONDENSER

DATE ANALYZED: 6/19/85

CAL ID: 20421-3RI

	AMOUNT FOUND (ng)	DETECTION LIMIT (ng)
FURANS		
Total TCDF	73	-
2,3,7,8-TCDF	40	-
Total PCDF	18	-
1,2,3,7,8-PCDF	ND	4.8
2,3,4,7,8-PCDF	ND	4.8
Total HCDF	ND	5.8
1,2,3,4,7,8-HCDF	ND	5.8
Total HpCDF	ND	7.0
1,2,3,4,6,7,8-HpCDF	ND	7.0
1,2,3,4,7,8,9-HpCDF	ND	7.0
Total OCDF	ND	9.5
DIOXINS		
Total TCDD	ND	2.7
2,3,7,8-TCDD	ND	2.7
Total PCDD	ND	17
1,2,3,7,8-PCDD	ND	17
Total HCDD	ND	6.8
1,2,3,4,7,8-HCDD	ND	6.8
Total HpCDD	ND	9.1
1,2,3,4,6,7,8-HpCDD	ND	9.1
Total OCDD	97	-

ND = Not Detected
RX = Re-extraction

RI = Reinjection

PREPARED BY: Jil

APPROVED BY: 6/20/85

DATE: 6/20/85

california Analytical Laboratories, Inc.

POLYCHLORINATED DIOXIN/FURAN ANALYSIS

TICKET NO: 20487

EXHIBIT B

CLIENT ID: COMPOSITE (DT-4B-B Filled
Impingers, DT-4B-B Probe Line)

DATE ANALYZED: 4/19/85

CAL ID: 20487-3,-4

	AMOUNT FOUND (ng)	DETECTION LIMIT (ng)
FURANS		
Total TCDF	11	-
2,3,7,8-TCDF	4.3	-
Total PCDF	1.0	-
1,2,3,7,8-PCDF	0.24	-
2,3,4,7,8-PCDF	0.17	-
Total HCDF	0.041	-
1,2,3,4,7,8-HCDF	0.041	-
Total HpCDF	ND	0.041
1,2,3,4,6,7,8-HpCDF	ND	0.041
1,2,3,4,7,8,9-HpCDF	ND	0.041
Total OCDF	ND	0.10
DIOXINS		
Total TCDD	5.8	-
2,3,7,8-TCDD	ND	0.99
Total PCDD	ND	0.036
1,2,3,7,8-PCDD	ND	0.036
Total HCDD	ND	0.049
1,2,3,4,7,8-HCDD	ND	0.049
Total HpCDD	ND	0.48
1,2,3,4,6,7,8-HpCDD	ND	0.48
Total OCDD	ND	0.20

ND = Not Detected
RX = Re-extraction

RI = Reinjection

PREPARED BY:

APPROVED BY:

DATE:

California Analytical Laboratories, Inc.

POLYCHLORINATED DIOXIN/FURAN ANALYSIS

TICKET NO: 20487

EXHIBIT C

CLIENT ID: DT-4B-B Resin

DATE ANALYZED: 4/19/85

CAL ID: 20487-5

	AMOUNT FOUND (ng)	DETECTION LIMIT (ng)
FURANS		
Total TCDF	ND	0.044
2,3,7,8-TCDF	ND	0.044
Total PCDF	0.038	-
1,2,3,7,8-PCDF	ND	0.0082
2,3,4,7,8-PCDF	ND	0.0082
Total HCDF	ND	0.0047
1,2,3,4,7,8-HCDF	ND	0.0047
Total HpCDF	ND	0.036
1,2,3,4,6,7,8-HpCDF	ND	0.036
1,2,3,4,7,8,9-HpCDF	ND	0.036
Total OCDF	ND	0.062
DIOXINS		
Total TCDD	ND	0.37
2,3,7,8-TCDD	ND	0.37
Total PCDD	ND	0.037
1,2,3,7,8-PCDD	ND	0.037
Total HCDD	ND	0.051
1,2,3,4,7,8-HCDD	ND	0.051
Total HpCDD	0.26	-
1,2,3,4,6,7,8-HpCDD	0.26	-
Total OCDD	5.8	-

ND = Not Detected
RX = Re-extraction

RI = Reinjection

PREPARED BY:

APPROVED BY:

DATE:

California Analytical Laboratories, Inc.

POLYCHLORINATED DIOXIN/FURAN ANALYSIS

TICKET NO: 20373

EXHIBIT D

CLIENT ID: COMPOSITE (DT-1S 2/26-2/27,
DT-1S-BRR)

DATE ANALYZED: 3/18/85

CAL ID: 20373-4,-7

	AMOUNT FOUND (ng)	DETECTION LIMIT (ng)
FURANS		
Total TCDF	ND	0.0091
2,3,7,8-TCDF	ND	0.0091
Total PCDF	ND	0.0058
1,2,3,7,8-PCDF	ND	0.0058
2,3,4,7,8-PCDF	ND	0.0058
Total HCDF	ND	0.014
1,2,3,4,7,8-HCDF	ND	0.014
Total HpCDF	ND	0.16
1,2,3,4,6,7,8-HpCDF	ND	0.16
1,2,3,4,7,8,9-HpCDF	ND	0.16
Total OCDF	ND	0.13
DIOXINS		
Total TCDD	ND	0.40
2,3,7,8-TCDD	ND	0.40
Total PCDD	ND	0.15
1,2,3,7,8-PCDD	ND	0.15
Total HCDD	ND	0.056
1,2,3,4,7,8-HCDD	ND	0.056
Total HpCDD	ND	0.19
1,2,3,4,6,7,8-HpCDD	ND	0.19
Total OCDD	16	-

ND = Not Detected
RX = Re-extraction

RI = Reinjection

PREPARED BY: JW

APPROVED BY: 1/24

DATE: 6/25/85

TABLE 4
Polychlorinated Dibenzofuran and Dibenzodioxin Summary

Date	Time	ID#	Type	Volume (ft ³)	Location	Total PCDF	Total Detection Limit (ng)	Total PCDD	Total Detection Limit (ng)
2-27-85	1531-1731	DT-1S	Baseline	87.05	Stack	0.03	0.73	18.60	2.09
3-8-85	0955-1155	DT-2S	Normal	85.22	"	2.12	0.79	5.20	4.12
3-8-85	0955-1155	DT-3S	Blank	-	"	ND	0.47	ND	2.96
3-12-85	1418-1618	DT-4S	Low Oxygen	86.05	"	ND	0.75	ND	5.22
3-14-85	1300-1500	DR-5S	"	87.75	"	ND	0.86	0.89	4.77
3-13-85	1035-1050	DT-6S	Blank	-	"	ND	0.69	ND	4.23
2-28-85	0912-1112	DT-1B	Baseline	83.47	Boiler	3.94	0.95	1.30	5.85
3-8-85	1024-1224	DT-2B	Normal	82.65	"	74.56	28.25	97.00	41.63
3-12-85	1430-1630	DT-3B	Low Oxygen	83.10	"	2.65	0.74	ND	4.10
3-14-85	1235-1444	DT-4B	"	80.52	"	12.08	0.40	11.86	3.20

not being injected with the spent acid. The sample consisted almost entirely of the one isomer OCDD.

Discussion

The "semi-volatile" resin train and "volatile" bag sample analyses indicated that the regeneration furnace provided high DE of "spike" compounds and minimal PIC formation. Emission rates are presented in Tables 5a through 5b. High DEs were observed during all tests (>99.999%), even during the attempt to simulate a "low O₂" failure condition. Thus, it is not surprising that little correlation was observed among the available continuous analyzer monitors (CO and O₂) and either DE of POHCs or formation of PICs. Generally speaking when the DEs were very high, the concentrations of contaminants were near the noise level of the sampling and analytical method, as indicated by statistically insignificant differences among the spiked ("normal") and unspiked ("baseline") samples.

The possibility of infiltration of ambient air between the dust collector exit and the stack sampling point was high because of the design of the system. Ambient air samples taken in the vicinity of the plant were about the same level as concentrations measured in the stack, with the exception of elevated levels of dichloroethane, dichloropropane and tetrachloroethane in bag samples BS-16S, 18S, and 19S and trichlorotrifluoroethane in BS-24B, 26B, 38S, and 40S. Concentrations of the former three compounds observed in bag samples drawn at the boiler exit on the same day also appeared to be elevated (BS-24B, 26B). An insufficient number of bags were analyzed to draw statistically valid comparisons. Because no corresponding duplicate bags were analyzed, it was not possible to rule out contamination in those few cases. However,

TABLE 5a
Emission Rates (micrograms/second)

ARB NO.	Date	Time	Test Condition	CARB TET	1,2,4 TCB	1,1,1 TCA	PCP
RT-1S	2-27-85	1428-1528	Baseline	2.8E+00	<2.9E+00	2.1E+01	3.8E+00
RT-2S	2-27-85	1620-1720	"	6.4E+00	<2.9E+00	1.8E+1	3.4E+00
RT-3S	2-28-85	0948-1148	"	5.3E+00	<1.4E+00	6.7E+00	<4.8E-01
RT-4S	2-28-85	0948-1148	"	2.1E+00	<1.4E+00	3.5E+00	<4.7E-01
RT-5S	3-1-85	0910-1110	"	1.1E+00	<1.4E+00	4.5E+00	1.4E+00
RT-6S	3-1-85	0916-1116	"	7.7E-01	<1.4E+00	7.5E+00	9.1E-01
RT-7S	3-5-85	1423-1523	Normal	3.1E+00	<2.9E+00	1.5E+01	2.5E+00
RT-8S	3-5-85	1430-1530	"	4.6E+00	<2.8E+00	2.4E+01	1.9E+00
RT-9S	3-6-85	1048-1348	"	1.7E+00	<1.5E+00	4.6E+00	1.9E+00
RT-10S	3-6-85	1048-1248	"	2.5E+00	<1.4E+00	7.8E+00	1.1E+00
RT-11S	3-7-85	1218-1418	"	n.a.	<1.4E+00	n.a.	n.a.
RT-12S	3-7-85	1215-1415	"	1.2E+00	<1.4E+00	1.9E+00	<4.6E-01
RT-14S	3-12-85	1118-1318	Low Oxygen	7.9E-01	3.2E+01	6.3E+00	<4.7E-01
RT-15S	3-12-85	1116-1317	"	1.3E+00	4.0E+01	6.8E+00	9.7E-01
RT-16S	3-14-85	1002-1202	"	1.6E+00	3.0E+01	7.2E+00	<4.8E-01
RT-17S	3-14-85	1000-1200	"	3.2E+00	3.0E+01	6.3E+00	1.8E+00

TABLE 5b

ARB NO.	Date	Time	Test Condition	Emission Rates (micrograms/second)				
				CARB TET	1,2,4 TCB	1,1,1 TCA	PCP	
RT-1B	2-27-85	1407-1607	Baseline	1.8E-01	<1.5E+00	2.0E+00	<5.1E-01	
RT-3B	3-1-85	0846-1056	"	1.8E-00	3.5E+00	2.0E+00	1.0E+00	
RT-4B	3-1-85	1313-1513	"	3.9E-01	<1.4E+00	1.4E-01	<4.8E-01	
RT-5B	3-5-85	1321-1533	Normal	7.4E+00	1.4E+01	1.0E+01	<5.4E-01	
RT-6B	3-6-85	1106-1322	"	1.1E+01	1.3E+01	1.4E+00	<5.5E-01	
RT-7B	3-7-85	1229-1429	"	4.3E+00	4.2E+00	7.3E+00	7.3E-01	
RT-8B	3-12-85	1115-1334	Low Oxygen	1.5E+00	1.9E+01	2.4E+00	1.3E+00	
RT-9B	3-14-85	0948-1201	"	2.7E+01	9.1E+01	3.0E+01	<5.7E-01	

based on the pattern of occurrences of elevated concentrations, contamination is an unlikely explanation as the cause of elevated concentrations.

The only outstanding pattern which appeared to be present in the data collected were the 1,2,4 trichlorobenzene results. The consistency of the duplicate analyses, good resin train recoveries and low field blanks were all indicative of high quality data. There appeared to be a distinct and statistically significant increase of stack emissions of TCB during the runs marked "low O_2 ". Too few points were available for a valid statistical test of boiler TCB concentrations, though the same trend was observed. The logarithm of the TCB penetration has been plotted against the logarithm of (CO/CO_2) in Figure 1. Lines joining the data points are indicative of data taken from duplicate trains. The arrows drawn on the data points indicate that concentrations were at detection limits reported by the analyst, thus penetrations may have been lower than indicated. It was not meaningful to attempt a correlation with such a small data set. In fact based upon results of laboratory tests there was sufficient reason to believe that a correlation, would not exist in general [3]. Rather, increases in CO concentration precede the occurrence of increased POHC penetration [4]. In these tests an increase in CO also appeared to have preceded penetration of a refractory POHC, TCB, in the synthetic "spike" waste.

It should be noted again that the term "low O_2 " is a misnomer in the sense that the condition was not based upon an analyzer reading, but rather upon a visual determination of the flame condition by the furnace operator. (The O_2 concentration was determined to be higher by continuous analyzer measurement in some of the "low O_2 " tests than during

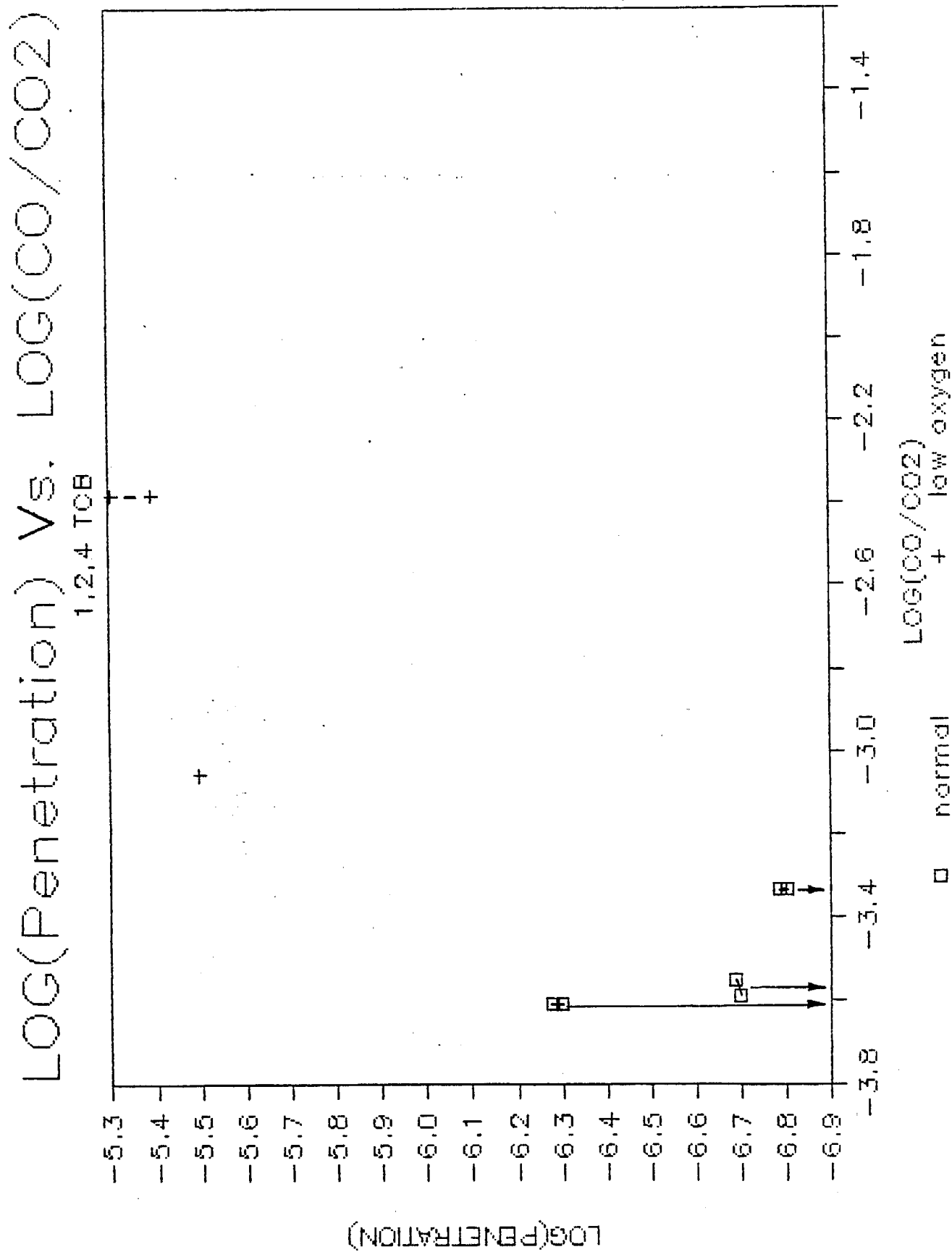


Figure 1 Logarithm of penetration versus logarithm of ratio of CO to CO₂.
Downward arrows indicate samples at analytical detection limits.

the "normal" and "baseline" runs!) Visual determination is not a desirable condition as there is little or no feedback provided to the furnace operator by the oxygen analyzer and the operator does not observe the flame continuously. Because CO concentrations were observed to increase during the "low O₂" runs, it would appear that the system should be equipped with at least one continuous CO monitor in addition to the O₂ monitor.

Polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) were detected in three of the samples at levels above detection limits. The emission rates are presented in Table 6. Two samples were drawn at the boiler exit, and concentrations in the corresponding stack samples were either not detectable or were close to detection limits. Furthermore, the isomers detected were not the same. The larger quantities of PCDFs and PCDDs were obtained during a "normal" run with a mixture of spiked synthetic waste and spent acid waste (DT-2B). Although there was no apparent reason for higher emissions, it should be pointed out that no continuous CARB CO analyzer data were available for comparison. The half hourly "instantaneous" CO concentrations recorded by the furnace operator did not give any indication of an upset having occurred, but such an occurrence cannot be ruled out. Average CO levels for the day did not appear to be higher than during other periods. No corresponding bag or resin samples were available for direct comparison with the dioxin/furan sample, DT-2B.

The second sample for which appreciable levels of PCDDs and PCDFs were detected at the boiler (DT-4B, 3/14/85) was drawn during a "low O₂" condition. As indicated in the previous discussion, increased penetration of TCB was observed under similar conditions. However, no detec-

TABLE 6

Polychlorinated Dibenzofuran and Dibenzodioxin Emissions

Date	Time	ID#	Type	Total Emission Rate PCDF (ng/min)	Total Emission Rate PCDD (ng/min)
2-27-85	1531-1731	DT-1S	Baseline	4.1	2735
3-8-85	0955-1155	DT-2S	Normal	332.4	815
	0955-1155	DT-3S	Blank	--	--
3-12-85	1418-1618	DT-4S	Low Oxygen	<114.4	<794
3-14-85	1300-1500	DT-5S	"	<140.1	<778
3-13-85	1035-1050	DT-6S	Blank	--	--

table levels of PCDDs or PCDFs were observed during the other "low O₂" test (DT-3B, 3/12/85). Although it appears that the CARB CO data for 3/12/85 were higher than on 3/14/85, the furnace operator's records indicate exactly the reverse situation. Thus, the sampling point for CO should be taken into careful consideration when issuing the permit.

The one stack sample (DT-1S) in which a significantly elevated level of a PCDF or PCDD was detected, consisted almost entirely of octachlorodibenzodioxin (OCDD). The sample was drawn during a "baseline" run when presumably low levels of chlorinated organics, based upon the qualitative GC/MS analysis, were being fed to the furnace. Its appearance is an anomaly for which there is no apparent explanation. No simultaneous boiler sample was drawn. CARB continuous CO analyzer data were low during the test (less than about 30 ppm) and the Stauffer CO readings were only at the 100 ppm level. It is not possible to rule out contamination or the release of OCDD or other compounds from the quench water. Presumably OCDD would be primarily associated with particulate matter at the temperature of the stack gas. The level of particulate matter measured in the stack was fairly consistent throughout all the tests. A PCDF/PCDD analysis of the particulate matter collected by the corresponding method 5 train might provide some confirmation of the elevated level observed in DT-1S, i.e., if no OCDD were to be associated with the particulate matter, then contamination would be a likely explanation.

The fact that TCB penetrated to the stack and was not removed effectively by the acid regeneration process suggests that other non-soluble POHCs and PICs exiting the boiler are also capable of penetrating to the stack. Although PCDFs and PCDDs appear to have had lower penetration

through the process (perhaps they were removed with the particulate matter by the electrostatic precipitators), assuring high DE in the furnace would appear to be more desirable than relying upon the additional particle control systems to achieve acceptable DE. Soluble PICs might be removed with the "quench water". It would be prudent to collect and analyze the "quench water" to determine whether any compounds are leaving the process through that stream, and whether it could have served as a source of PCDFs and PCDDs in the stack.

Recommendations

The technical difficulties in conducting extensive tests of waste incinerators which are integral portions of industrial processes were evident during this series of tests. Panel recommendations to determine an "operating envelope", to simulate atomizer failure and to test the effects of the furnace water injection system were not carried out, in part, out of concern upon the part of the operator that a process upset would occur. Because these tests were not performed, it is difficult to make recommendations regarding operating permit conditions for the non-criteria organic pollutants. Nevertheless, some conservative suggestions are offered.

1. Since the effect of the cooling water injection system was not tested, the permit should not allow use of water injection as a method of reducing furnace temperature.
2. Since atomizer failure was not tested, it is suggested that some type of "fail-safe" system should be installed to detect such a condition

and that this be made a condition of the permit.

3. A continuous CO analyzer readout should be installed on the system as a condition of the permit. It would not seem to be acceptable to have periodic visual examination of flame condition as the primary method for checking the adequacy of combustion conditions. We infer from the resin train results that of all the readily measurable variables, elevated CO level was indicative of occurrence of reduced DE in the furnace.
4. It is not possible to specify a definitive acceptable level for CO as a permit condition on the basis of the recent test results. It appeared that increased penetration of TCB occurred at a CO level as low as about 100 ppm (based on periodic Stauffer CO measurements, 3/12/85 "low O₂" test). However, CARB continuous analyzer records indicate that a CO excursion, >4800 ppm, occurred during the period that the resin samples were being drawn. Average levels of CO during the 3/14/85 "low O₂" test were 75 to 100 ppm on the CARB analyzer and 220 to 375 ppm according to the Stauffer records. Further testing to reconcile the continuous analyzer data should

be carried out to determine whether sampling location or instrument malfunction was at fault. While such tests are conducted, it would be desirable to define a "map" of acceptable visual flame condition with the continuous CO analyzers. Such tests could be run quickly at little additional expense and without the need for "spiked waste". The additional data could assist the permit engineer with selection of an acceptable maximum CO level.

5. The minimum temperature at the front and back sensors of the furnace were about 1250°F and 1800°F respectively. Temperature did not appear to explain the penetration of any of the POHCs through the furnace and these minimum levels appeared to be adequate to decompose the POHCs for the given furnace residence time.
6. The minimum O₂ level observed during any of the tests was about 1.4% (Stauffer O₂ analyzer, dust chamber). The corresponding CARB O₂ analyzer reading was about 7%. It is recommended that a level of about 1.5% (Stauffer analyzer) should be considered a minimum independent of the CO analyzer reading since no correlation of O₂ could be

demonstrated with DE of any of the POHCs. Again, analyzer location may be quite important because of infiltration of air into the system and additional testing to reconcile the continuous analyzers would be worthwhile.

7. Steps should be taken to increase the quantity and quality of data captured during the intensive sampling periods. Little information regarding PIC formation was generated because so few of the bag samples were actually analyzed and a valuable opportunity was lost.
8. Continuous gas analyzers should be used whenever samples are being drawn for POHC or PIC studies. Lack of CO and THC measurements during the 3/8/85 "normal" test, make it impossible to know whether a change in furnace condition was responsible for the increased formation of PCDF and PCDD observed.
9. Analyses for PCDF and PCDD in the particulate matter recovered by the EPA method 5 trains and in gas cooler quench water samples might still be of value. If funds are available, analyses should be carried out even though no special sample preparation was attempted and no quality control or blanks are available for comparison.

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